THE METAL—IRON

ALLOYS OF IRON RESEARCH
Monograph Series

In Preparation

THE METAL–IRON

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PREFACE

This monograph, the sixth in order of publication and the fifth of the regular series, is a review of available information on the preparation and properties of metallic iron of high purity and is, therefore, a basis for the other monographs of the series. The true foundation would be the fundamental properties of pure iron, *i.e.*, of iron which contains no trace of any other element, but such iron has never been prepared, at least in useful quantities; consequently the properties of pure iron have not been determined. The best available approximation of the properties of pure iron is supplied by the properties of the purest irons on record but, according to the authors' definition, these are the properties of high-purity iron, not of pure iron. Throughout the text, the expression pure iron is avoided; even the purest irons so far produced are considered to be of high purity but not pure.

In this monograph, as in previous books of the regular series, temperatures are given in degrees centigrade, except in those portions of the text which are of especial interest to the engineer or the practical steel worker, in which case conversions have been made to the nearest 5 degrees Fahrenheit. In the chapters on the preparation of high-purity iron current densities are given in both metric and English units.

In the chapters on mechanical properties definitions have been adopted which were used in previous monographs of the series. The property variously reported in the literature as elastic limit, proportional limit, or yield point has been termed *yield strength*, unless it was determined in accordance with the definitions of elastic limit or proportional limit proposed by the American Society for Testing Materials (*Proceedings*, v. 31, part 1, 1931, pp. 602–604). In all cases the term used by the original investigator has also been given in a footnote. Most of the values termed yield strength were determined by the "drop-of-beam" method.

The appended bibliography refers mainly to articles which have been consulted in the original, although in a few cases it was necessary to rely upon abstracts. In such cases both the original and abstract references are cited. References are arranged in the bibliography chronologically by year of publication and alphabetically by author for each year. Patents are cited in the text when desired information could be found in patent specifications and not elsewhere; no attempt at a comprehensive search of patent literature has been made.

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PART I

PREPARATION OF HIGH-PURITY IRON

CHAPTER I

LABORATORY PRODUCTION OF ELECTROLYTIC IRON

Aqueous Electrolytes: Sulphate Baths—Aqueous Electrolytes: Chloride Baths—Other Aqueous Electrolytes—Organic Electrolytes—Fused Electrolytes—Authors' Summary

The methods by which iron of high purity has been prepared are of two general types: electrolytic methods, whereby iron is produced by electrolytic deposition, and chemical methods, whereby purified iron compounds are reduced or decomposed to give the metal, or solid or molten iron is further purified by chemical treatment.

Electrolytic processes may be classified as refining processes when impure forms of iron, used as anodes, are refined electrolytically, and as extraction processes when solutions of iron salts, obtained usually by chemical treatment of iron ores, are electrolyzed with insoluble anodes. Extraction processes have usually been devised for use on a commercial scale and are, therefore, considered in Chapter II in connection with the commercial manufacture of electrolytic iron. Electrolytic refining and chemical methods of purification have been employed both for laboratory experimentation and for production on a larger scale.

The ensuing discussion of electrolytic processes will be divided according to the type of electrolyte used.

A. AQUEOUS ELECTROLYTES: SULPHATE BATHS

Of the three types of electrolytes, aqueous, organic, and fused, that have been used in the electrolytic refining of iron only the first is of importance. The organic and fused electrolytes, while possibly of scientific interest, have had no practical applications.

1. Historical Review.—Although the preparation of iron by electrodeposition was reported as early as 1831 by Becquerel[2] and was investigated in 1846 by Bockbuschmann and Liet[4] and by Böttger,[5] and in 1848 by Ryhiner,[7] the product seems to have been more or less of a scientific curiosity for several decades.

Roberts[31] stated that specimens of electrolytic iron were exhibited by Feuquières at the Paris Exposition in 1867 and that Garnier in 1858 had patented a process for preparing electrotypes by deposition of iron on copper. Improvements in Garnier's process were proposed by Meidinger[11] and others, but the only early use of the process seems to have been at the Russian Mint where bank notes were printed from electrolytic-iron electrotypes prepared by a process developed by Klein[17,21] in 1869. The properties of the iron prepared by Klein's method were described by Lenz[23] in 1871. Following a visit to the laboratories of the Russian Mint, Roberts-Austen[39] in 1887 gave further details of the Klein process. Other early work on the preparation of electrolytic iron is that of Beetz,[12] who prepared material for magnetic tests in 1860, and Krämer,[14] who in 1861 prepared, from a ferrous chloride electrolyte, iron which he stated was sufficiently soft to be cut with a knife. Varrentrapp[19] in 1868 experimented with a mixed ferrous chloride ferrous sulphate electrolyte. Classen and von Reis[32] in 1881 developed a method for the determination of iron by electro-deposition. The early work on the preparation of iron by electrodeposition was reviewed by Volger[29] in 1874, Roberts[31] in 1875, Guillet[304] in 1915, and Escard[397] in 1919.

In developing processes for the preparation of electrolytic iron the production of material of the highest purity possible has not always been the aim. Where it has been the intention to develop a process for "steel facing" electrotypes, building up undersized or worn parts of machinery, or manufacturing iron tubes or iron sheets, etc., freedom from such defects as gas pits, non-uniformity, and non-adherence has been the goal, rather than freedom from impurities. When a process was developed with the intent or hope of use on a commercial scale, economic considerations required the use of high current density with high current efficiency and a long-lived bath, even though the conditions thus imposed were incompatible with the attainment of the highest purity. In evaluating processes of electrodeposition the order of merit necessarily depends upon whether the criterion is excellence of physical structure, economy of operation, or purity of product.

In addition to the references cited throughout the text, information regarding the electrodeposition of iron is contained in

books on electroplating, particularly in the books by Schlötter,[222] Pfanhauser,[484,935] Hughes,[517] and Blum and Hogaboom.[548] Hughes,[437] in an excellent review of the electrolytes proposed for the deposition of iron, found that the aqueous solutions used could, with few exceptions, be divided into three groups, namely (1) those in which iron was present in the form of ferrous sulphate, (2) those with iron present as ferrous chloride, and (3) those with both sulphate and chloride present. This convenient classification will be used here in considering the methods which have been suggested for the preparation of electrolytic iron.

2. Ferrous Sulphate Baths.—The process developed by Klein for "steeling" electrotypes was satisfactory, the original process or the modification of it by Maximowitsch[133] in 1905 having been used at the Russian Mint, according to Escard,[397] at least up to the time of the revolution in 1917. In addition to the information published by Jacobi[21] and Klein[17] and contained in British patent 2,456 of 1869, descriptions of the process have been given by Roberts-Austen[30] and by Haber.[79] The electrolyte was an aqueous solution containing 5 g. each of ferrous sulphate and magnesium sulphate per liter. Bags of magnesium carbonate were suspended in the bath to keep it neutral. The principal drawback to the process was the low current density permissible, 0.1 to 0.2 amp. per sq. dm. (0.9 to 1.9 amp. per sq. ft.), which resulted in very slow deposition. Haber[79] stated that six weeks were required to obtain a deposit 2 mm. in thickness; and that the deposits had a tendency to peel unless a rotating cathode was used, which also permitted use of higher current densities, up to 0.42 amp. per sq. dm. (3.9 amp. per sq. ft.).

Maximowitsch,[133] who worked with Klein, described a modification of the Klein electrolyte which he stated gave deposits more suitable for printing plates than those from the original Klein bath, being tougher and less brittle. The modified bath was prepared as follows: a 6-liter vessel was filled with a solution which contained 200 g. of ferrous sulphate crystals and 5 g. of Epsom salts per liter. Two iron anodes, 20 × 15 cm., were suspended in the electrolyte; between them was the cathode, a copper plate lightly silvered and iodized to facilitate removal of the deposit. Twenty-five g. of sodium bicarbonate were added to the solution, causing the formation of a voluminous precipitate which gradually settled, leaving the solution clear. At the same

time a yellow scum, which formed on the surface of the electrolyte, gradually oxidized to a brown film which protected the bath from further oxidation. During the course of the electrolysis 20 to 25 g. of bicarbonate were added twice weekly until 186 g. of the salt had been added. A current density as high as 0.6 amp. per sq. dm. (5.6 amp. per sq. ft.) could be used but the best results were obtained with 0.3 amp. per sq. dm. (2.8 amp. per sq. ft.). The low current density permissible with this bath limited it to uses where the rate of deposition was not an important item. Eventually the bath deteriorated; however, Maximowitsch found that passing pure carbon dioxide through the solution would restore its former excellence and permit the bath to be used for long periods of time.

Maximowitsch stated that smooth flexible deposits, free from gas pits and nodules and having a tensile strength of 5180 kg. per sq. cm. (73,700 lb. per sq. in.) could be obtained from this bath. Although Pfanhauser[484, p. 669] was not successful in obtaining flexible deposits, Ryss and Bogomolny[149] and Hughes[437] confirmed the statement of Maximowitsch. Ryss and Bogomolny found the bath satisfactory for the production of thick, homogeneous deposits of iron. Addition of both magnesium sulphate and sodium bicarbonate to the ferrous salt was necessary to obtain satisfactory deposits; addition of either one alone did not suffice.

Iron deposited from electrolytes containing magnesium salts, such as the Klein or Maximowitsch solutions, contained an appreciable amount of magnesium, according to Lee.[190] This observation was confirmed by Kremann and Lorber[307] who found that iron deposits, which contained as much as 3 per cent of magnesium, could be obtained. According to modern ideas, this magnesium must have been present in the form of magnesium salts; metallic magnesium could not be present in electrolytic iron, at least in any such amounts.

A solution of ferrous sulphate, saturated at room temperature but used at 90°C. (195°F.) with a current density of 2 amp. per sq. dm. (18.6 amp. per sq. ft.), was preferred by Lee.[190] The addition of about 2.5 g. of sulphuric acid per liter was recommended.

In German Patent 308,543, February 7, 1908, Schlötter proposed an electrolyte which contained 150 g. of ferrous sulphate and 100 g. of sodium sulphate per liter and was used at 100°C. (210°F.) with a current density of 2.1 amp. per sq. dm. (20 amp.

per sq. ft.). Free acid was neutralized with sodium carbonate. Hughes[437] criticized the process as likely to give trouble because of excessive evaporation at the temperature specified. Also, if the electrodeposition was not continuous, difficulty was caused by the crystallization of salts when the bath cooled.

3. Ferrous Ammonium Sulphate Baths.—Neuburger stated[124] that he and von Klobukow deposited iron, for analytical purposes, from a ferrous sulphate solution which contained ammonium oxalate. An item of interest in connection with their work is Neuburger's statement that the deposited iron would not rust, even though kept under conditions most favorable for rusting.

Hoepner and Klie, whose work was reported by Arndt,[252] prepared electrolytic iron from a solution containing 308 g. of ferrous sulphate and 50 g. of ammonium sulphate per liter of water. A current density of 3 amp. per sq. dm. (28 amp. per sq. ft.), bath temperature of 70 to 80°C. (160 to 175°F.), and bath voltage of 0.75 volt were used.

Electrodeposition as a means of preparing "pure" iron for use in standardizing permanganate solutions was studied by Skrabal.[112,126] He prepared purified ferrous ammonium sulphate by recrystallization from acid solutions, also by neutralizing ferric ammonium sulphate solution with ammonium carbonate and boiling. The precipitate which formed, after filtering and washing, was dissolved in pure sulphuric acid. Ammonium sulphate was added to the solution and the ferric salts were reduced by electrolysis between platinum electrodes. The ferrous salt was then twice recrystallized or was fractionally precipitated with alcohol. A solution of this purified salt was electrolyzed with platinum electrodes, and the cathode of deposited iron was subsequently made the anode in a second electrolysis. No analysis of the product was given.

In another paper Skrabal[125] reported that two forms of electrolytic iron could be produced. One form, which he called *A*-iron, was obtained from a ferrous salt solution with an iron anode, low voltage, and low current density. The product was silver-white in color, compact, and extremely hard. The second type, *B*-iron, was prepared with a platinum anode in an electrolyte containing ferrous iron in a complex form, with high voltage, and high current density. This form of electrolytic iron was grayish in color and was less compact and less hard than *A*-iron.

Since the conditions of deposition could be varied at will, a variety of kinds of electrolytic iron was possible with properties more or less similar to *A*-iron or *B*-iron, according to Skrabal. He considered that a difference in structure was responsible for the differing types of iron and that the softening of electrolytic iron upon annealing was due to a change in structure, the loss of hydrogen being incidental and not, as is generally supposed, the cause of the change in properties.

4. Work of Burgess and Hambuechen.—Burgess and Hambuechen[120] are credited with being the first to produce electrolytic iron in quantity. Publication in 1904 of the results of their investigation gave a decided impetus to large-scale production. The electrolyte was a solution of ferrous ammonium sulphate, stated by Johnston[723] to contain 275 g. of this salt per liter of water. Müller[196] used baths containing 15, 30, and 50 per cent by weight of ferrous ammonium sulphate and found the 30 per cent solution the most satisfactory. The conditions specified by Burgess and Hambuechen were: current density 0.65 to 0.86 amp. per sq. dm. (6 to 8 amp. per sq. ft.) at the cathode, slightly less at the anode, bath voltage less than 1 volt, bath temperature 30°C. (85°F.). The rate of deposition was 1 g. per watt-hr. or 2.2 lb. per kw-hr. They were able to make continuous runs of four weeks, the deposit reaching a thickness of $\frac{3}{4}$ in.; the electrolyte could be kept in good condition for at least two months. Information as to the acidity of the bath was not given in their paper. Hughes[437] stated that he was able to get good results with their process only when the bath was maintained slightly acid. In addition to Müller and Hughes, Lee,[190] Amberg,[172,204] Pfaff,[198] and Ryss and Bogomolny[149] investigated the method of Burgess and Hambuechen.

5. Work of Amberg and of MacFadyen.—The purpose of Amberg's work[172] was the preparation of 1 kg. of pure iron a week for scientific uses. He used as electrolyte solutions of ferrous ammonium sulphate with concentrations from 15 to 45 g. of iron per liter and finally adopted a concentration of 26 g. of iron per liter as giving the best results. His anodes were two bars of Krupp iron covered with linen bags and laid in the center of a stoneware tank which had a capacity of 30 liters. Two cathodes of either copper or sheet iron were hung one on each side of the anodes. The electrolyte was covered with a layer of paraffin to

furnish protection from oxidation. The current density used was from 0.2 to 0.65 amp. per sq. dm. (1.9 to 6 amp. per sq. ft.); with the higher current density agitation of the electrolyte was necessary. The temperature of Amberg's electrolyte was not stated in his paper but Tucker and Schramm[226] assumed that it was room temperature. To improve the purity of his product Amberg re-electrolyzed, using the cathodes from the first electrolysis for anodes in the second. He gave no analysis of his product other than the statement that it was over 99.9 per cent pure. He concluded that absolutely pure iron could not be obtained electrolytically, since the deposit can inclose two kinds of substances: particles of the electrolyte and colloidal impurities from the anode. Tucker and Schramm[226] investigated Amberg's process and found it superior, from the standpoint of workability and physical character of the deposit, to Kern's sulphate bath and to the Maximowitsch modification of Klein's bath but inferior to the chloride bath of Kern.

MacFadyen[406] used a ferrous ammonium sulphate solution as an electrolyte from which to deposit iron for "building up" purposes. Good physical properties are essential in iron deposited for this purpose, smoothness, adherence, and homogeneity being of paramount importance. Although MacFadyen was interested primarily in these properties rather than in the purity of the iron, his results are of value in any consideration of the sulphate bath.

The concentration of the bath, he found, could be varied between wide limits and yield satisfactory deposits, but a concentrated solution allowed the use of a higher current density and speeded up the rate of deposition. However, with concentrations between 100 and 300 g. of ferrous ammonium sulphate per liter there was somewhat more pitting than with concentrations between 50 and 100 g. per liter or between 305 and 410 g. per liter (saturation). The latter range of concentration allowed the use of current densities up to 1.7 amp. per sq. dm. (16 amp. per sq. ft.) as against a maximum permissible current density of 0.54 amp. per sq. dm. (5 amp. per sq. ft.) for concentrations below 300 g. per liter. The baths in all cases were operated at room temperature.

In his acidity experiments MacFadyen worked with a solution containing 350 g. of ferrous ammonium sulphate per liter and

found that increased acidity decreased the current efficiency from about 98 per cent at an acidity of 0.001 N, to 95 per cent at 0.005 N and 90 per cent at 0.01 N.   Acidities of from 0.003 N to 0.03 N gave satisfactory deposits with the bath at room temperature; with the bath at 60°C. (140°F.) acidities of from 0.01 N to 0.02 N were preferred.

With concentrated solutions the current density that could be used depended upon the temperature of the bath, the maximum value, measured in amp. per sq. ft., being always slightly higher than the temperature, stated in °C., up to 50°C. (120°F.). Above that temperature the employable current density rose rapidly.

A summary of the preferred conditions for a ferrous ammonium sulphate bath according to MacFadyen, is: concentration, 350 g. per liter; acidity, 0.01 N to 0.02 N; temperature, 60°C. (140°F.); current density, 6.4 to 10.7 amp. per sq. dm. (60 to 100 amp. per sq. ft.).   As cleanliness of the cathodes is essential for good adherence, MacFadyen included in his paper his method of cleaning them, also his methods of testing for adherence.

6. Comparisons of Sulphate Baths. A series of papers published by Watt[41] in 1887–1888 gave results of his investigation of the suitability of 44 different electrolytes for the deposition of iron.   Both organic and inorganic salts of iron were used.   Watt concluded that the following salts, given in the order of his preference, were satisfactory for the plating of iron:

1. Ferrous ammonium sulphate
2. Ferrous sulphate and magnesium sulphate
3. Ferrous sulphate and ammonium chloride
4. Ferrous sulphate

Ryss and Bogomolny[149] could not get satisfactory results with the sulphate bath when used at elevated temperatures and recommended a bath composed of 70 g. of ferrous ammonium sulphate per liter, to be used at room temperature with a current density of 0.5 amp. per sq. dm. (4.7 amp. per sq. ft.).

Electrolytes containing ferrous sulphate, ferrous sulphate plus sodium sulphate, and ferrous chloride plus sodium chloride were investigated on a laboratory scale by Kern.[179]   The ferrous sulphate solution contained 400 g. of the crystallized salt per liter, equivalent to an iron content of about 80 g. per liter. Currents of 1.1 to 2.2 amp. per sq. dm. (10 to 20 amp. per sq. ft.)

were used, requiring potentials of 1.15 to 1.4 volts at 20°C. (70°F.) and 0.8 to 0.98 volt at 50°C. (120°F.).

The ferrous sulphate sodium sulphate solution contained 300 g. of ferrous sulphate and 210 g. of Glauber's salt per liter, equivalent to an iron content of about 60 g. per liter and a sodium content of about 30 g. per liter. At current densities of 1.1 to 2.2 amp. per sq. dm. (10 to 20 amp. per sq. ft.) the potentials required were from 0.95 to 1.2 volts at 20°C. (70°F.) and from 0.6 to 0.8 volt at 50°C. (120°F.). Kern found that the deposits from these two sulphate baths were about equal in quality; both were smoother than the deposits from the chloride bath but were of less desirable structure, being harder and more crystalline. Hence Kern preferred the chloride electrolyte.

Müller[190] investigated the Maximowitsch bath and the Burgess and Hambuechen bath. With the former a current density of 0.5 amp. per sq. dm. (4.7 amp. per sq. ft.) was the maximum that would give good results, although 0.8 amp. per sq. dm. (7.4 amp. per sq. ft.) could be used with the latter at room temperature, which he found preferable to a higher temperature. The deposits from the sulphate electrolytes contained total impurities as high as 0.10 per cent and sulphur as high as 0.01 per cent, the sulphur content in one case being higher than that of the anode iron. Müller concluded that the sulphate bath was useless where deposits containing little or no sulphur were desired. Pfaff[198] stated that, while Müller's conclusions might be true for iron deposited under his conditions, they did not hold for electrolytic iron from sulphate baths in general. Pfaff obtained iron from a sulphate electrolyte with a sulphur content as low as 0.00018 per cent, and concluded that the sulphur content of iron deposited from ferrous sulphate electrolytes never reached 0.001 per cent. Although most workers with the sulphate bath have not obtained the high sulphur contents reported by Müller, it usually has been above the maximum set by Pfaff. Hughes[437] expressed doubt that Müller's results proved that the sulphate bath was inferior to the chloride for the preparation of "pure" iron. A peculiarity of Müller's iron was its unusually high carbon content; from an anode having 0.075 per cent carbon, he obtained electrolytic iron with 0.072 per cent carbon. In another experiment the iron produced contained 0.069 per cent carbon although the anode material had but 0.035 per cent. This was despite

the fact that the anodes were contained in porous cups which tend to prevent migration of carbonaceous material to the cathode. Müller's excessively high carbon and sulphur contents, as compared with those obtained by other workers who used similar solutions and conditions, raise doubt as to the accuracy of his analytical methods.

Pfaff[219] investigated the methods of Merck (chloride), Burgess and Hambuechen, and Lee. Of the three, he preferred Lee's sulphate bath but obtained better results by working it at 70°C. (160°F.) than at the temperature Lee preferred, 90°C. (195°F.). Pfaff did not see any advantage in replacing ferrous sulphate with the more expensive ferrous chloride as with the latter salt he did not obtain such uniform deposits as with the sulphate. His best results were obtained with a 2 N ferrous sulphate solution that was 0.01 N with respect to sulphuric acid. The bath was used at 70°C. (160°F.) with a current density of 2 amp. per sq. dm. (18.6 amp. per sq. ft.). He stressed the importance of acidity and found that with decreasing iron content in the electrolyte the deposits became less dense and homogeneous. To remove hydrogen bubbles he blew a stream of air against the cathode, a procedure criticized by Hughes[437] as productive of oxidation.

7. Effect of Operating Conditions.—The effect of conditions of deposition on the current efficiency and on the properties of the deposited metal was studied by Lee.[190] For sulphate baths operated at a current density of 1.6 amp. per sq. dm. (15 amp. per sq. ft.), Lee found that increasing the temperature of the bath increased the current efficiency, improved the structure, and decreased the hydrogen content of the deposited metal, as is shown in the following results:

FERROUS SULPHATE ELECTROLYTE, 2.2 TO 2.3 N

Temperature		Hydrogen in deposit, per cent	Current efficiency, per cent
°C.	°F.		
18	65	0.085	32
37	100	0.039	43
55	130	0.024	61
75	165	0.0096	83

At a constant bath temperature, the hydrogen content of the iron decreased during the course of the electrolysis, each successive layer of iron containing less hydrogen than the preceding layer, as the following results illustrate:

FERROUS SULPHATE ELECTROLYTE AT 37°C. (100°F.)

Time of Deposition, Hr.	Hydrogen Content of Iron, Per Cent
2.5	0.061
3	0.053
4	0.043
5	0.039
6	0.036

Increasing the current density increased the rate of deposition but also increased the hydrogen content. Iron deposited from a ferrous sulphate solution at 37°C. (100°F.) with a current density of 1.6 amp. per sq. dm. (15 amp. per sq. ft.) had a hydrogen content of 0.033 per cent; with a current density of 3.2 amp. per sq. dm. (30 amp. per sq. ft.), the hydrogen content was 0.053 per cent.

With increase in acidity of the solution, within certain limits, the deposits showed better adherence and less tendency to exfoliate; the hydrogen content was lowered but the current efficiency was greatly decreased, as is shown by the following results:

FERROUS SULPHATE ELECTROLYTE,
2.2 TO 2.3 N AT 37°C. (100°F.)

Acidity	Current efficiency, per cent	Hydrogen content, per cent
0.01 N	89.1	0.077
0.05 N	52.0	0.053
0.10 N	17.7	0.034

The effect of variation of hydrogen ion concentration, current density, and temperature on the hardness of electrodeposited metals was investigated by MacNaughton.[570] He found that the general effect of an increase in acidity was to cause an increase in hardness, as is shown by the following results from a ferrous ammonium sulphate electrolyte (75 g. per liter) used at room

temperature with a current density of 0.5 amp. per sq. dm. (4.7 amp. per sq. ft.):

Hydrogen ion concentration, pH range.........	5.7 to 5.5	4.5 to 4.2	3.8 to 3.6	3.5 to 3.3
Brinell hardness.	140	167 to 195	225 to 244	256 to 281

The hydrogen ion range of 5.7 to 5.5 was obtained by addition of ferrous carbonate, the others by addition of sulphuric acid. By use of a more concentrated electrolyte (325 g. of ferrous ammonium sulphate per liter) higher current densities could be used. The effect of increasing the current density was to increase the hardness of the iron:

Current density, amp. per sq. ft.....	5	10	15	20
Potential difference, volts..........	0.52	0.72	0.96	1.26
Brinell hardness..................	182	229	283	354

The above results were obtained with the bath at 19°C. (65°F.). With the bath at 41°C. (105°F.) and with a current density of 5.4 amp. per sq. dm. (50 amp. per sq. ft.), iron with a Brinell hardness of 240 was obtained. The Fischer-Langbein bath (chloride), operated at 95°C. (205°F.) with a current density of 10.7 amp. per sq. dm. (100 amp. per sq. ft.), yielded deposits which had a Brinell hardness as low as 180.

MacNaughton concluded that increase in hydrogen ion concentration and current density tended to harden the deposits, whereas increase in bath temperature tended to soften them, and that by judicial adjustment of these factors iron deposits could be obtained of various degrees of hardness ranging from 140 to 360 Brinell. Microscopic examination of the deposits indicated that hardness was associated with fineness of crystalline structure.

8. Summary of Work with Sulphate Baths.— Electrolytic iron has been produced from sulphate baths by a number of investigators. Solutions of ferrous sulphate were used in the early investigations, but the limited solubility of this salt so restricted the permissible current density that the deposition of iron was exceedingly slow. Additions of magnesium sul-

phate, sodium bicarbonate, sodium sulphate, ammonium oxalate, and ammonium sulphate improved the electric efficiency of the ferrous sulphate electrolyte but tended to contaminate the deposited iron. Better success seems to have been obtained from solutions of ferrous ammonium sulphate than from the other sulphate baths; a solution of this salt was used by Burgess and Hambuechen, who were the first to produce electrolytic iron in quantity. The selection of electrolyte and of operating conditions varied with different investigators and was largely dependent upon the aims of the investigation, which were either to produce iron of the utmost purity, or to produce large amounts of electrolytic iron of reasonable purity, or for various electroplating uses such as the building up of worn parts or the coating of printing plates. Essential details of a number of these sulphate solutions are summarized in Table 1.

Advantages of the sulphate baths, in general, include the use of a cheap electrolyte; possibility of operation at relatively low temperatures; and low susceptibility to oxidation of both the bath and the deposited iron. The product from the sulphate baths is comparable in purity with that from chloride baths; iron in which the total of fixed impurities was considerably less than 0.1 per cent, according to the reported analyses listed in Table 3 (page 29), has been produced from both types of baths but sufficient data are not available for the accurate estimation of the optimum purity obtainable or of the average purity that may be expected. Many investigators were more interested in the physical properties than in purity of product; consequently analyses were not made. In other cases determinations of only a limited number of impurities were made. It has been rather common practice to subtract the sum of the determined impurities from 100 per cent, and to call this difference the iron content or the "purity" of the material. To the authors it does not appear that this practice is permissible for electrolytic iron, since in practically all cases the analyses are incomplete. For this reason the analyses in Table 3 are summarized as "Total Fixed Impurities Determined" rather than as purity of the product. Attention is called to the analysis of open-hearth ingot iron (page 72) which shows that a number of elements ordinarily disregarded in the analysis of ferrous materials may be associated with iron in detectable amounts.

TABLE 1.—SULPHATE SOLUTIONS FOR THE ELECTRODEPOSITION OF IRON

Investigator	Date	Electrolyte	Acidity	Current density, amp. per sq. dm.	Current density, amp. per sq. ft.	Temperature	Remarks
Klein[17,31]	1867	Ferrous sulphate, 50 g., magnesium sulphate, 50 g., water, 1 liter	Neutral with MgCO₃	0.1 to 0.2	0.9 to 1.9	Room	Thin deposits for "steel" facing
Hoepner and Klie[332]	1895	Ferrous sulphate, 467 g., ammonium sulphate, 750 g., water, 1500 cu. cm.	Weakly acid	3	28	70 to 80°C. (160 to 175°F.)	Thin deposits. Used porous diaphragm
Neuburger and von Klobukow[184]	1890	Ferrous sulphate and ammonium oxalate	Neutral with ammonia	....	....	....	For analytical purposes. Deposit analyzed 99.9 per cent iron
Strabel[112,124]	1904	Purified ferrous ammonium sulphate	....	....	....	Room	Pure iron for standardizing solutions
Burgess and Hambuechen[188]	1904	Ferrous ammonium sulphate	....	0.65 to 0.85	6 to 8	....	For iron refining. Product over 99.9 per cent iron
Maximowitsch[183]	1905	Ferrous sulphate, 200 g. per liter	NaHCO₃ added	0.3	2.8	Room	For "steel" facing
Lee[199]	1906	Ferrous sulphate, saturated at room temperature	0.05 N	2	18.6	90°C. (195°F.)	Bath covered with paraffin. Solution agitated. Pfaff[26] preferred a temperature of 70°C. (160°F.) with this bath
Ryss and Bogomolny[118]	1906	Ferrous ammonium sulphate, 70 g. per liter	....	0.5	4.7	Room	Higher temperatures gave poor deposits
Amberg[117,204]	1908	Ferrous ammonium sulphate, 182 g. per liter	....	0.2 to 0.65	1.9 to 6	Room	Agitation necessary at higher current densities
Kern[179]	1908	Ferrous sulphate, 400 g. per liter	H₂SO₄ to clear	1.1 to 2.2	10 to 20	20 and 50°C. (70 and 120°F.)	Deposit good but inferior to chloride deposit
Kern[179]	1908	Ferrous sulphate, 300 g. plus sodium sulphate, 210 g. per liter	H₂SO₄ to clear	1.1 to 2.2	10 to 20	20 and 50°C. (70 and 120°F.)	Deposit good but inferior to chloride deposit
Pfaff[26]	1910	Ferrous sulphate, 2 N	0.01 N	2	18.6	70°C. (160°F.)	Iron containing less than 0.001 per cent sulphur

The requirements for the production of electrolytic iron of utmost purity, which differ markedly from requirements for quantity production, have been summarized by Escard[397] as follows: Anodes must be of the purest obtainable iron, should be cleaned at frequent intervals, and should be surrounded, when in use, with porous cups; the cathode must be carefully freed from grease and scale; the electrolyte must be free from carbon compounds and must be renewed daily; the bath should be protected against oxidation; the current density must not be too high; and both the electrodes and the electrolyte must be stationary.

On the other hand, a successful process for quantity production necessitates the use of high current densities at high current efficiencies. These requirements are fulfilled by rotation of the cathode at a speed determined by the current density used, by circulation of the anode electrolyte, and by careful control of temperature and concentration of the bath and of the voltage and current density. The presence of free acid in the electrolyte produces a tendency toward exfoliation of the deposit; the bath should withstand extended use without renewal.

B. AQUEOUS ELECTROLYTES: CHLORIDE BATHS

9. Chloride Solutions.—In 1861 Krämer[14] electrodeposited iron from a ferrous chloride solution and obtained a product which was sufficiently soft to be cut with a knife, in contrast to the hardness usually associated with unannealed electrolytic iron.

In an attempt to prepare sulphur-free iron for use in the Marsh test, Thiele[52] electrolyzed, with platinum electrodes, a ferrous chloride solution containing 400 g. of anhydrous ferrous chloride per liter of water. This solution was previously digested with the purest iron obtainable to precipitate the baser metals. Barium chloride was then added to precipitate any sulphate present. After filtering, 50 cu. cm. of glacial acetic acid per liter of solution were added. As the iron obtained oxidized easily, it was quickly washed with water, alcohol, and ether and dried in vacuum over sulphuric acid. Despite his precautions, Thiele found that from 0.0048 to 0.0075 per cent of sulphur was present in the iron.

The investigation of Hicks and O'Shea[66] attempted to produce for scientific uses iron as free as possible from impurities.

Because of the possibility of sulphur contamination with the sulphate bath, a chloride electrolyte was chosen. When a ferrous chloride solution containing no other salts was used, a slimy precipitate soon coated the cathode. Addition of hydrochloric acid prevented this precipitation but caused gas evolution and pitting; addition of ammonium chloride in the proportion of two molecules of the ammonium salt to each molecule of ferrous chloride prevented the formation of the precipitate and allowed the bath to be worked in the neutral condition. It was concluded that the presence of acid was harmful, a conclusion with which Hughes[437] seems both to agree and to disagree.* A current density of 0.15 to 0.17 amp. per sq. dm. (1.4 to 1.6 amp. per sq. ft.) was the maximum that could be used with satisfactory results. The cathode was a carefully cleaned copper sheet backed with glass. The combined action of air and electrolyte at the point where the cathode entered the solution caused solution of the copper, which then precipitated on the neighboring iron deposit. Painting all parts of the cathode, except where the iron was to be deposited, prevented this contamination. The carbon from the anode settled to the bottom of the cell as a black sludge but the sulphur of the anode oxidized and dissolved. To prevent the accumulation of sulphur in sufficient quantity to contaminate the deposit, the anode liquor was discarded twice daily and the anode compartment (a porous pot) was refilled with fresh electrolyte which had been shaken with powdered iron to reduce any ferric salt. Use of an automatic scraper to remove gas bubbles and thus avoid formation of gas pits was not successful. Hicks and O'Shea suggested that automatically raising the cathode from the solution at frequent intervals would cause the hydrogen bubbles to break and thus solve the difficulty although Watt[41] had previously questioned the value of this procedure on account of the atmospheric oxidation which ensues therefrom. Hicks and O'Shea[66] stated that their own analyses and those of Prof. Arnold showed that sulphur was not present in determinable amounts but that a trace of chlorine and some occluded gases were present in the iron.

Merck patented a process of iron deposition (German Patent 126,839, February 12, 1900), the salient points of which were the

* The agreement is discussed on page 188, the disagreement on page 199, of Hughes' article.

use of a concentrated ferrous chloride solution at a temperature of at least 70°C. (160°F.) with either a moving cathode or agitation of the electrolyte. A current density of 3 to 4 amp. per sq. dm. (28 to 37 amp. per sq. ft.) was recommended. Pfaff[219] tested this solution with unsatisfactory results, such as non-adherence and gas pitting or treeing, depending upon the acidity. Due to the high temperature and ensuing loss of water by evaporation, frequent additions of water were necessary, causing sudden changes in temperature and stirring up the anode sludges.

A ferrous chloride electrolyte recommended by Ryss and Bogomolny[149] was composed of equal weights of ferrous chloride crystals and water. This gave good results when used at a temperature of 60 to 70°C. (140 to 160°F.) with a current density of 0.4 amp. per sq. dm. (3.7 amp. per sq. ft.). They found it preferable to raise the current density gradually to a maximum.

The chloride electrolyte used by Kern[179] contained 285 g. of crystalline ferrous chloride and 102 g. of sodium chloride per liter of solution, equivalent to an iron content of about 8 per cent and a sodium content of about 4 per cent. The addition of 1 part of concentrated hydrochloric acid to each 100 parts of electrolyte was necessary to prevent formation of a precipitate. The presence of the acid caused liberation of hydrogen, which, together with the formation of ferric salts by atmospheric oxidation, resulted in comparatively low current efficiency (93.45 per cent). Kern suggested that a covering of vaseline or paraffin on the bath would prevent formation of ferric salts by oxidation, thus removing the necessity for the presence of acid and permitting the bath to be used more nearly neutral with consequent better current efficiency. In the discussion of his paper, Kern stated that increase of the sodium content to 7 per cent resulted in better deposits. Of the six baths tested by Tucker and Schramm[226] the ferrous chloride sodium chloride bath of Kern gave the best results. They found the best temperature range for this bath to be between 50 and 70°C. (120 and 160°F.).

A ferrous chloride electrolyte containing 300 g. of ferrous chloride per liter was preferred by Müller.[196] Lower concentrations resulted in split and stripped deposits, greater concentrations gave rise to blistered surfaces and increased gas pitting. As regards temperature, Müller is at variance with the majority

of workers with the chloride bath. He preferred to work the bath at room temperature, claiming that higher temperatures gave deposits which were non-homogeneous and which oxidized readily. He found the optimum current density to be 0.7 amp. per sq. dm. (6.5 amp. per sq. ft.).

Vie[410] investigated both the sulphate and the chloride baths and preferred the chloride solution of the following composition: ferrous chloride 285 g., sodium chloride 162 g., water to make 1 liter. The bath was used at a temperature between 50 and 70°C. (120 and 160°F.) with a current density of 1.6 amp. per sq. dm. (15 amp. per sq. ft.). He stated that his product, which was a gray, non-crystalline deposit, was over 99.9 per cent pure, hydrogen being the only detectable impurity.

10. The Fischer-Langbein Bath.— The solution usually designated as the Fischer-Langbein bath was developed largely by A. Fischer, a series of patents (U. S. Patents 992,951, May 23, 1911; 992,952, May 23, 1911; 987,318, March 21, 1911; 1,001,770, August 29, 1911; German Patents 212,994, 1908; 228,893, 1909; 230,876, 1909) being granted in the period from 1908 to 1911 to cover the process. The bath was essentially an improvement of the one patented by Merck (German Patent 126,839, February 12, 1900); the improvement consisted principally in the addition of a hygroscopic salt such as calcium, aluminum, or magnesium chloride, or a salt which forms a hygroscopic compound with ferrous chloride (sodium chloride for example). One of the recommended compositions and the one which is usually designated as "Fischer's electrolyte" was: ferrous chloride crystals 450 g., calcium chloride 500 g., water 750 g. The presence of the hygroscopic salt allowed the use of a high temperature for deposition [90 to 110°C. (195 to 230°F.) is specified in one patent, 60 to 80°C. (140 to 175°F.) in another] without serious loss of water by evaporation. The high working temperature of the bath permitted the use of high current density (up to 20 amp. per sq. dm. or 186 amp. per sq. ft.) with correspondingly rapid deposition; it also caused high current efficiency to be obtained, as was shown by Lee.[190] The presence of the salt also seemed to inhibit to some extent the oxidation of the ferrous chloride. Because of the high current density employable and the high current efficiency obtained, the process is well suited to the commercial refining of iron.

Hughes[471,472] made a thorough investigation of the ferrous chloride calcium chloride bath and stated that it was one of the best available for the deposition of iron. Hughes found that it was necessary, after dissolving the salts, to skim off the froth and to filter or to siphon after settling. Glass, porcelain, or enameled iron was suitable for a container. The current density employable depended upon the temperature. The bath could not be worked at room temperature but current densities up to 26 amp. per sq. dm. (240 amp. per sq. ft.) could be used at 90°C. (195°F.) and up to 31 amp. per sq. dm. (288 amp. per sq. ft.) at 110°C. (230°F.). The addition of acid reduced the cathode efficiency and made the deposit hard and brittle with outgrowths and gas pits. Addition of a small amount of alkali improved the deposits, but sufficient alkali to cause formation of a precipitate was harmful. Neither agitation of the solution nor movement of the cathode was necessary. Under proper conditions of deposition the iron was malleable, not brittle as electrodeposited iron usually is. Duisberg[250] stated that the Fischer-Langbein iron was very soft, being little harder than aluminum, with magnetic properties superior to those of silicon iron. Analyses of the product showed an iron content from 99.942 per cent, as given by Elmen in the discussion of Hughes'[437] paper, to 99.995 per cent as reported by Pfanhauser.[484, p. 672]

Kelsen, in British Patent 306,151, February 16, 1928, proposed an electrolyte consisting of ferrous chloride and two other salts such as calcium chloride and potassium chloride, the combined weights of the two salts being greater than the weight of either necessary to cause saturation.

The novelty of the electrodeposition process devised by Duhme[552] lay rather in the design of the cell than in the electrolyte, which was a modification of one of Fischer's solutions (ferrous and magnesium chlorides). The cathode was a rotating solid cylinder, placed in the center of the cell. Surrounding it was a perforated cylindrical metal shell which acted as a secondary cathode. Just outside this shell were the anodes of steel or cast iron. The area of the anodes was about four times that of the main cathode. In the bottom of the cell, sealed in glass tubes, were a number of permanent magnets to hold particles falling from the anodes and thus prevent contamination of the deposit by these anode particles. Air was blown against the

primary cathode to remove hydrogen bubbles. A small alternating current flowed between the anodes and the secondary cathode; according to Duhme, this served to prevent contamination of the deposit by phosphorus. At the temperature used, slightly below 100°C. (210°F.), a current density of 10 amp. per sq. dm. (93 amp. per sq. ft.) was used; the current efficiency was 92 per cent. Duhme's analysis of his product showed an iron content (by difference) of 99.994 per cent. No mention was made of the magnesium content, although from the work of Lee[190] and of Kremann and Lorber[307] the presence of this impurity would be expected.

11. Work at the National Bureau of Standards (U.S.A.) and the National Physical Laboratory (England).—To prepare pure iron for scientific uses, Cain, Schramm, and Cleaves[349] at the National Bureau of Standards electrolyzed a ferrous chloride solution, 250 to 300 g. per liter, made by dissolving ingot iron (99.78 per cent Fe) in pure hydrochloric acid, the solution being prepared as nearly neutral as possible. The current density used was from 0.5 to 0.7 amp. per sq. dm. (4.7 to 6.5 amp. per sq. ft.), the bath being at room temperature. Cylindrical anodes of ingot iron were contained in porous cups, the resulting cathode deposit being somewhat lower in impurities than that obtained without the use of porous cups. Analysis of the anode sludge indicated an accumulation of copper and manganese in the anode cell. Sheet iron cathodes were used. Atmospheric oxidation resulted in the precipitation of basic ferric salts. Sealing the top of the cell with a glass plate and replacing the air by purified carbon dioxide did not improve the result, particularly as the carbon content of the product seemed to be higher when carbon dioxide was present above the bath. The material was undoubtedly contaminated to a slight extent by the basic salts but such impurities were largely reduced or volatilized in the subsequent melting operation. The total of fixed impurities in the iron prepared by this method was from 0.024 to 0.026 per cent, of which 0.011 per cent was cobalt and nickel. Iron prepared on a somewhat larger scale with an electrolyte containing 233 g. per liter of ferrous chloride and 103 g. per liter of sodium chloride, using a current density of 0.3 to 0.4 amp. per sq. dm. (2.8 to 3.7 amp. per sq. ft.), contained

0.033 per cent of fixed impurities. In both cases the product, after washing, rusted badly.

Tritton and Hanson[585] at the National Physical Laboratory, using the procedure of Cain, Schramm, and Cleaves, obtained a product which, they stated, was free from silicon, sulphur, phosphorus, and manganese and contained only a trace of carbon. They found it to have an oxygen content of 0.277 per cent, however, due to rusting which they were unable to prevent, although the greatest care was taken in washing and drying the material. The study of the preparation of high-purity iron was continued at the National Physical Laboratory, but only meager scraps of information are available subsequent to the report of Tritton and Hanson. According to various annual reports from the National Physical Laboratory, difficulty was encountered at one time or another from contamination by oxygen, phosphorus, and sometimes by carbon. The annual report for 1931 contained the statement that production of high-purity iron in ingots of about 5 lb. had been reduced to a routine operation, but the report for 1932 stated that small but measurable quantities of nickel, cobalt, and chromium (from the anode material) had been detected by spectroanalysis and that higher purity was desirable. According to recent information[1044, 1050.4] metal which contained 0.022 per cent nickel, 0.006 per cent carbon, 0.003 per cent chromium, 0.001 per cent phosphorus, 0.0008 per cent copper, 0.0005 per cent silicon, and no sulphur and manganese was considered to be about the best obtainable by electrodeposition; hence the electrolytic method has been abandoned, for the production of iron of the highest purity, in favor of decomposition of the ferrous chloride by means of steam with subsequent reduction of the oxide with hydrogen.

12. Effect of Operating Conditions.—The effect of varied conditions of deposition on the current efficiency and on the properties of the deposited metal was studied by Lee,[190] who found, for chloride baths as for sulphate baths, that increasing the temperature of the bath increased the current efficiency, improved the structure, and decreased the hydrogen content of the deposited metal. For a bath 2.2 N with respect to ferrous chloride, an increase in temperature from 37 to 75°C. (100 to

165°F.) increased the current efficiency from 46 to 82 per cent and decreased the hydrogen content from 0.058 to 0.018 per cent. In a ferrous chloride bath maintained at a temperature of 37°C. (100°F.) the hydrogen content of the deposited metal decreased progressively with time, from 0.076 per cent in the metal deposited during the first two or three hours to 0.058 per cent in that deposited during the sixth hour. An increase in current density tended to increase the hydrogen content of the deposited metal. A decrease in concentration of ferrous chloride in electrolytes 0.05 N with respect to hydrochloric acid decreased the hydrogen content of the iron deposited at a current density of 1.6 amp. per sq. dm. (15 amp. per sq. ft.) but also decreased the current efficiency, as follows:

Temperature		Current efficiency, per cent, in ferrous chloride electrolyte		
°C.	°F.	4.6 N	2.3 N	0.8 N
18	65	49.6	21.0	9.0
37	100	46.3	30.4	12.7
55	130	62.7	46.0	21.1
75	165	81.7	64.6	34.0

Hughes[437] preferred to use the chloride bath in the neutral condition, with addition of alkali chloride to prevent oxidation, and considered unnecessary the use of organic salts or addition agents.

In a study of the effect of conditions of deposition on the hardness of the deposited metal, MacNaughton[670] found that acidification of a ferrous chloride electrolyte was accompanied by increased hardness of the deposited iron. The Brinell hardness of iron from a bath with no added acid was 199; addition of hydrochloric acid until the solution was 0.002 to 0.003 N with respect to hydrochloric acid, increased the Brinell number to 344.

A recent reference[1039] has been noted to an Austrian attempt to prepare "pure" iron by electrolysis of a filtered solution of ferrous chloride, with controlled current density and controlled temperature. The process was stated to be still in the experimental stage.

13. Other Investigations.—Hineline's investigation[514] in 1923 was to determine the best electrolyte and conditions to deposit iron successfully on irregularly shaped rubber articles. The bath suitable for such a purpose must have a high "throwing" power so that crevices as well as raised surfaces of the object will be coated with iron. A ferrous ammonium sulphate bath was soon rendered useless by organic materials extracted from the rubber. The deposit from the Fischer-Langbein bath pitted and corroded badly as did that from a simple ferrous chloride solution. Reducing compounds as addition agents were tried, chromous chloride
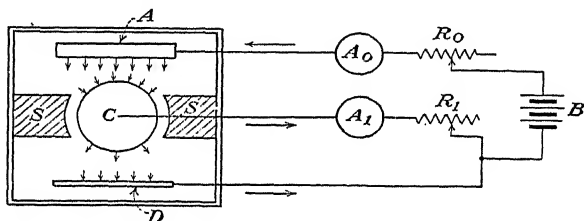

Fig. 1.—Two-compartment cell for the electrodeposition of iron. (*Hatta.*[565])

and hydroquinone giving the most satisfactory deposits. The following bath was finally selected as best for the purpose:

To each liter of a solution of equal parts of ferrous chloride and calcium chloride, saturated at 30°C. (85°F.), were added 20 g. of chromous chloride and 5 g. of hydroquinone. This bath was used at a temperature between 60 and 70°C. (140 and 160°F.); current densities as high as 8 amp. per sq. dm. (75 amp. per sq. ft.) could be employed. The acidity of the bath was about right if good grades of ferrous and calcium chlorides were used.

The rubber articles were given a conducting surface by varnishing and coating with graphite. It was found necessary to "stop off" the raised surfaces with varnish until the deposit had formed in the crevices, when the raised surfaces were given a conducting coating and the deposition continued.

With the belief that electrolytic iron, deposited free from hydrogen, would be sufficiently soft and flexible to permit stripping from the cathode without breaking, Hatta[565] devised a cell utilizing anodic polarization for the removal of the hydrogen. In its simplest form, as shown in Fig. 1, there was the anode *A*, the rotating cathode *C* (called the main cathode), and an auxiliary cathode *D*. Separators *S* of insulating material were fitted close

to the main cathode C and served to minimize the leakage of
current from anode A through the electrolyte to auxiliary cathode
D.   The current entered the cell at A (total current) and passed
through the electrolyte to that side of the main cathode C which
was towards A.   Part of the current left the cell directly from C
(effective current), part went from C through the electrolyte to
the auxiliary cathode D, where it left the cell (auxiliary current).
A_0 and A_1 were ammeters; R_0 and R_1 were variable resistances
for controlling the current.   Figure 2 illustrates a four-compart-
ment cell having the main anodes A and the auxiliary cathodes D
in alternate compartments.   A six-compartment cell, having
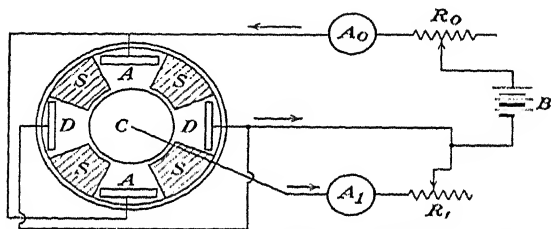three main anodes and three auxiliary cathodes, was also used
by Hatta.

FIG. 2.—Four-compartment cell for the electrodeposition of iron.   (*Hatta.*[555])

As the main cathode C rotated, there was deposition of iron
on the side towards A; at the same time the side towards D
acted as an anode and there was dissolution of part of the
deposited iron with removal of hydrogen by the accompanying
anodic polarization.   Thus, the surface of the main cathode, as
it rotated, underwent alternate cathodic deposition of iron and
anodic polarization for the removal of hydrogen.   Under proper
conditions, iron nearly free from hydrogen could be produced.

As electrolytes, sulphate, chloride, and mixed sulphate-chloride
solutions were tried, the preferred solution containing ferrous
chloride, 4.6 N (455 g. of $FeCl_2.4H_2O$ per liter) and sodium chlo-
ride, 2.3 N (135 g. per liter).   Potassium chloride or calcium
chloride could be substituted for the sodium chloride.   Acidity
between 0.005 N and 0.03 N was necessary with the chloride
solution; sulphate solutions required an acidity of 0.05 N.   The
best working temperature for the chloride solution was 70°C.
(160°F.).   The total current was kept at about twice the effective

current. The relation between current density, speed of cathode rotation, and cycles per revolution was complicated. Using a main cathode 5 cm. in diameter and a current density of 2.5 amp. per sq. dm. (23 amp. per sq. ft.), Hatta found that with the two-compartment cell (one cycle per revolution), 900 r.p.m. were necessary to give a good product; with the four-compartment cell (two cycles per revolution) and with the six-compartment cell (three cycles per revolution) a speed of at least 600 r.p.m. was required.

With Hatta's process two types of electrolytic iron were produced simultaneously, a practically hydrogen-free product on the main cathode and approximately an equal amount of ordinary electrolytic iron on the auxiliary cathode. The material from the main cathode had a hydrogen content of less than 0.0002 per cent, that from the auxiliary cathode contained 0.0108 per cent hydrogen. Hatta gave the following analysis of his product: carbon 0.036 per cent, silicon 0.002 per cent, sulphur 0.008 per cent, and traces of manganese, phosphorus, and arsenic. No analysis was given of the material used for anodes but, judging by the carbon content of the product, it was not particularly pure. The electrolytic iron deposited on the rotating cathode was sufficiently soft and flexible to permit its being stripped in sheets. Nevertheless, despite its low hydrogen content, its physical and magnetic properties did not approach those of "pure" iron until it had been annealed at 900°C. (1650°F.), indicating to Hatta that the deposited material was structurally different from annealed iron. His theory was that iron deposited in the presence of hydrogen had a structure different from the normal structure of "pure" iron, and that the removal of the hydrogen at ordinary temperatures, as by anodic polarization, did not change the structure to normal, annealing at 900°C. (1650°F.) being necessary to cause this change in structure.

14. Summary of Work with Chloride Baths.—The conclusions of Escard[397] in regard to the varied requirements for the production of high-purity iron or for production on a commercial scale applied to chloride as well as to sulphate baths. Escard's conclusions were discussed in a previous section on sulphate baths, and need not be repeated here.

Available information regarding important chloride baths, for the laboratory preparation of electrolytic iron, is summarized in

TABLE 2.—CHLORIDE SOLUTIONS FOR THE ELECTRODEPOSITION OF IRON

Investigator	Date	Electrolyte	Acidity	Current density, amp. per sq. dm.	Current density, amp. per sq. ft.	Temperature	Remarks
Thiele[59]	1891	Ferrous chloride, 400 g. per liter	50 cu. cm. glacial acetic per liter	....	....	Room	Deposit contained 0.0048 to 0.0075 per cent sulphur
Hicks and O'Shea[66]	1895	Ferrous chloride, plus 5% NH₄Cl to form FeCl₂, 2 NH₄Cl	Neutral	0.15 to 0.17	1.4 to 1.6	Room	Deposit very pure
Ryss and Bogomolny[148]	1906	Ferrous chloride, 1000 g., water, 1 liter		0.4	3.7	60 to 70°C. (140 to 160°F.)	Raised current density gradually
Kern[177]	1908	Ferrous chloride, 255 g., sodium chloride, 102 g., water, to make 1 liter	Concentrated HCl, 10 cu. cm. per liter	1.1 to 2.2	10 to 20	20 and 50°C. (70 and 120°F.)	Deposit superior to deposits from sulphate baths. Current efficiency lower
Müller[190]	1909	Ferrous chloride, 300 g. per liter		0.7	6.5	Room	Deposits purer than from sulphate solutions
Cain, Schramm, and Cleaves[249]	1916	Ferrous chloride, 250 to 300 g. per liter	Neutral	0.5 to 0.7	4.7 to 6.5	Room	Fixed impurities, 0.024 to 0.026 per cent. Porous cups, no agitation
Cain, Schramm, and Cleaves[249]	1916	Ferrous chloride, 233 g., sodium chloride, 102 g., water to make 1 liter	Neutral	0.3 to 0.4	2.8 to 3.7	Room	Larger scale than above. Impurities 0.033 per cent
Vie[108]	1919	Ferrous chloride, 255 g., sodium chloride, 102 g., water to make 1 liter		1.6	15	50 to 70°C. (120 to 160°F.)	Product over 99.9 per cent iron
Hineline[310]	1923	Ferrous chloride and calcium chloride, equal parts saturated at 35°C. (95°F.). Hydroquinone and chromous chloride added	No acid added	10	93	Slightly below 100°C. (210°F.)	For depositing on irregular shaped articles
Duhme[352]	1924	Ferrous chloride and magnesium chloride, concentrated solution	No acid added	10	93	Slightly below 100°C. (210°F.); 70°C. (160°F.)	Special cell. Product 99.994 per cent iron
Merck (Ger. Pat. 126,839)	1900	Ferrous chloride, concentrated solution		3 to 4	25 to 37	70°C. (160°F.)	Agitation necessary. For iron refining
Fischer-Langbein (Ger. Pat. 212,994),	1908	Ferrous chloride, aq. 450 g., calcium chloride, 500 g., water, 750 cu. cm.	No acid added	10 to 20	93 to 186	90 to 110°C. (195 to 230°F.)	Deposit of high purity, hydrogen content low
Kalen (Brit. Pat. 306,151)	1928	Ferrous chloride, calcium chloride, potassium chloride		....	....	....	Greater concentration by using two conductivity salts

Table 2. Analyses of some of the iron produced from chloride baths are shown in Table 3.

TABLE 3.—REPORTED ANALYSES OF LABORATORY ELECTROLYTIC IRON

Process	Reference	Composition of product, per cent						Total of fixed impurities determined
		C	S	P	Mn	Si	Other impurities	
Sulphate baths								
Müller*.............	196	0.0720	0.0099	0.0042	0.0100	0.0079	....	0.1040
Müller†.................	196	0.0690	0.0078	0.0058	0.0039	0.0070	....	0.0935
C. F. Burgess.............	349	0.009	0.003	Trace	Trace	0.006	0.006 Cu	0.024
C. F. Burgess.............	141	0.012	None	0.004	None	0.013	0.072 H	0.029
C. F. Burgess.............	141	0.033	0.001	0.020	None	0.003	0.083 H	0.056
Chloride baths								
Müller.................	196	0.023	Nil	0.004	Trace	0.004	....	0.031
Müller*.................	196	0.0630	0.0024	0.0045	0.0090	0.0053	....	0.0842
Hicks and O'Shea..........	66	None	None	None	None	None	Trace Cl; small quantity of gases	Trace
Fischer-Langbein...........	484	0.0001	0.0001	0.0002	......	0.0001	0.0045	......
Cain, Schramm, and Cleaves‡	349	0.004	0.002	Trace	Trace	0.003	0.006 Cu; 0.011 Ni + Co	0.026
Cain, Schramm, and Cleaves§	349	0.004	0.006	Trace	Trace	0.008	0.006 Cu; 0.011 Ni + Co	0.035
Duhme‖.................	552	0.002	......	0.001	0.002	0.001	....	0.0051
Hatta‖.................	565	0.036	0.008	Trace	Trace	0.002	0.0002 hydrogen	0.046

* Anode impurities 0.186 per cent.

† Anode impurities, omitting slag, 0.095 per cent.

‡ With porous cup.

§ Without porous cup.

‖ Special cell.

Chloride baths, essentially aqueous solutions of ferrous chloride, have been used by a number of investigators, for the production of electrolytic iron. Additions of alkali or alkaline earth chlorides were frequently employed to decrease loss of water by evaporation and also to decrease oxidation of the electrolyte at the elevated temperatures necessary for efficient operation of the chloride bath. Most of the advantages claimed for the chloride baths, in comparison with sulphate baths, were due to the higher concentrations of iron obtainable as a result of the relatively large solubility of ferrous chloride in water.

High concentrations of iron increase the conductivity of the bath to some extent but the effect is less than that of small additions of the chlorides of sodium or calcium. On the other hand, the greatest electric efficiency for chloride baths is obtained only at relatively high temperatures, and both the bath and the deposited iron are unusually susceptible to oxidation.

The purity of the product of chloride baths is comparable to that of sulphate baths, but again it is impossible to state either the optimum purity obtainable or the average purity which might be expected. Attention is called to the fact that Cain, Schramm, and Cleaves[349] are the only investigators of those cited, who reported the presence of nickel and cobalt in their electrolytic iron, and are the only ones who reported examination of their product for the presence of these impurities. Such an amount of nickel and cobalt, if present in the electrolytic iron from other investigations, would constitute an appreciable addition to the total of impurities of these irons.

C. OTHER AQUEOUS ELECTROLYTES

15. Mixed Sulphate Chloride Solutions.· Meidinger[11] in 1859 and Varrentrapp[19] in 1868 proposed electrolytes composed of ferrous sulphate and ammonium chloride for use in "steeling" electrotypes, the presence of ammonium chloride, according to Varrentrapp, permitting more rapid deposition. An electrolyte containing 4 per cent of ferrous sulphate and 4 per cent of ammonium chloride was one of those used with satisfactory results by Burgess[230] at the University of Wisconsin. This bath could be worked continuously for several months with a current density of 0.66 to 1.1 amp. per sq. dm. (6 to 10 amp. per sq. ft.) at a potential of 1 volt, the current efficiency being nearly 100 per cent. Deposits up to 2 in. in thickness were produced with a purity reported to be as high as 99.97 per cent.

An electrolyte developed by Watts and Li[319] had the following composition: ferrous sulphate crystals 150 g., ferrous chloride crystals 75 g., ammonium sulphate 120 g., ammonium oxalate 6 g., and water to make 1 liter. The bath was used at room temperature with a current density of 1.07 amp. per sq. dm. (10 amp. per sq. ft.). Deposits from this bath were reported to be smoother than those from the sulphate bath and more rust resisting than those from simple chloride solutions. This

electrolyte was adopted by the Western Electric Company for use in the large-scale production of electrolytic iron for magnet cores as described in a subsequent section. Watts and Li gave no analysis of their product but Skowronski[582] stated that the material produced at the Western Electric plant had a purity of 99.97 per cent.

British Patent 119,200, April 26, 1918, was issued to Shepherd and Brazil, Straker and Company, for a bath consisting of ferrous sulphate, ammonium chloride, finely divided metallic iron, potassium bromide, and boric acid. This was intended for use in electroplating articles with iron. Arzano and Clerici (British Patent 114,305, February 26, 1918) proposed an electrolyte composed of 42 parts of ferrous sulphate and 50 parts of aluminum chloride dissolved in sufficient water to give a solution with a density of 30° Bé. This bath was to be used at a temperature of 100 to 105°C. (210 to 220°F.).

Hughes[437] compared the mixed chloride sulphate bath with the single chloride or sulphate baths and concluded that the mixed bath had no points of superiority over the single anion electrolyte and had certain disadvantages such as difficulty of control, not present in the simpler baths.

16. Summary of Data on Mixed Sulphate Chloride Baths.— Electrolytes containing both chloride and sulphate have been criticized on the grounds of being difficult to control, but nevertheless have been successfully employed for the production of electrolytic iron, in at least one case on something more than a laboratory scale. Details of some of the mixed sulphate chloride baths are summarized in Table 4.

17. Other Aqueous Solutions.—Böttger[5] in 1846 used a bath of soluble Berlin blue (ferric ferrocyanide) which, he stated, gave good results for "steel facing." Watt[41] found Böttger's bath inferior to the sulphate and chloride electrolytes.

The ferrous sulphocresylate bath, used at first by Cowper-Coles,[175] was abandoned according to Hughes[437] and to Palmaer and Brinell[288] in favor of the ferrous chloride bath with the sulphocresylate salt as an addition agent.

Ferrous fluosilicate solution was found by Kern[179] to be entirely unsatisfactory as silica collected on the cathode and made the deposit very brittle. Nevertheless, this solution was later patented by Harbeck (German Patent 288,660, January 16, 1914;

Swedish Patent 41,303, September 20, 1916) as an electrolyte for iron deposition.

Electrolysis of a solution of ferrous ammonium fluosilicate for 170 hr. with a current density of 1.1 amp. per sq. dm. (10 amp. per sq. ft.) at 26°C. (80°F.) gave a deposit which was dark gray, streaky, and very nodular, according to Watts and Li.[319] At the end of the deposition the cell was half full of a white precipitate. A ferrous fluoborate solution gave similar results.

TABLE 4.—MIXED SULPHATE CHLORIDE SOLUTIONS FOR THE ELECTRODEPOSITION OF IRON

Investigator	Date	Electrolyte	Current density, amp. per sq. dm.	Current density, amp. per sq. ft.	Temperature	Remarks
Meidinger[11]....	1859	Ferrous sulphate, 2 lb., ammonium chloride, 1 lb., water, 4 liters	....	....	Room	Used for "steel facing"
Varrentrapp[19]....	1868	Ferrous sulphate, 4 lb., ammonium chloride, 3 lb., water, 30 lb.	0.1 to 0.2	1 to 2	Room	Used for "steel facing"
C. F. Burgess[230].	1911	Ferrous sulphate, 200 g., ammonium chloride, 40 g., water, to make 1 liter	7 to 1.1	6.5 to 10	Room	Deposits up to 2 in. with a purity of 99.97 per cent
Watts and Li[319]...	1914	Ferrous sulphate, 150 g., ammonium chloride 75 g., $(NH_4)_2SO_4$, 120 g., + ammonium oxalate 6 g., water to make liter	1.1	10	Room	For iron refining
Arzano and Clerici (Brit. Pat. 114,-305).	1918	Ferrous sulphate, 4 parts, ammonium chloride, 50 parts, water to adjust to 30° Bé.			100 to 105°C (210 to 220°F.)	For iron refining
Shepherd and Brazil, Straker and Co., (Brit. Pat. 119,200).	1918	Ferrous sulphate, ammonium chloride, potassium bromide, and iron metal. Boric acid added				For electroplating with iron

Hineline[514] made a solution of ferrous sulphite by treating precipitated ferrous carbonate with sulphur dioxide. Upon electrolysis, no iron was deposited, a mass, apparently composed of ferric sulphate and ferrous sulphide, forming at the cathode.

The use of an iron sodium pyrophosphate solution for the electrodeposition of iron was proposed by Brand[44] in 1889.

Marino patented (British Patent 10,133, July 12, 1915) an electrolyte consisting of a strong solution of sodium pyrophosphate containing 10 per cent of phosphoric acid and 5 to 15 per cent of sulphanilic acid. This solution was to be prepared by a preliminary electrolysis with an iron anode. The use of ferrous silicofluoride or ferrous borosilicofluoride solutions for iron deposition was suggested by Plauson and Teschtschenko (British Patent 10,882, 1912). Schlötter · (German Patents 305,156, 1917; and 309,164, 1918) proposed the use of ferrous perchlorate solution.

Solutions of iron salts other than the sulphate or chloride have been tested for use as electrolytes in iron deposition, but none has been found to have any advantages over the two more common and cheaper salts and most have been distinctly inferior.

18. Addition Agents.—Strictly speaking, the term "addition agents" designates a class of substances which are added to the electrolyte, usually in relatively small quantities, for the purpose of improving the structure or appearance of the deposit but not for the purpose of controlling the hydrogen ion concentration of the solution or of increasing its conductivity. The ensuing discussion, however, will include additions of acids and conductivity salts and will also include additions of reducing compounds whose function is to prevent the formation of ferric ions.

The addition of small "doses" of citric or tartaric acid was recommended by Watt.[41] Vie[410] added citric and sulphurous acids together to prevent the formation of a basic precipitate. He found formic and oxalic acids to be unsatisfactory for this purpose. Kremann and Breymesser[381] found that the addition of citric acid to the Fischer-Langbein bath caused the current efficiency to drop from 99.46 per cent to 88.57 per cent. According to Lee,[190] the weak acids such as citric or boric act as buffers, that is, they serve as reservoirs of hydrogen ions, allowing the solution to be used with low hydrogen ion concentration but preventing alkalinity by furnishing hydrogen ions to replace those removed from solution by the reactions which occur during the course of the electrolysis.

Hineline[514] found hydroquinone and chromous chloride satisfactory for preventing the formation of ferric ions; sodium bisulphite was also effective. Vie[410] used sulphurous acid for the same purpose.

Ammonium oxalate is frequently added to the iron solution in the analytical determination of iron by electrodeposition; its use for this purpose was proposed by Classen and von Reis[32] in 1881. The solution used by Neuburger and von Klobukow in 1890 also contained ammonium oxalate, according to Neuburger.[124] Watts and Li[319] found this salt to be the most beneficial of the addition agents tested by them. Amberg,[204] however, believed the addition of ammonium oxalate to be useless, a conclusion with which Hughes[437] concurred. Hughes found that addition of oxalate caused a precipitate to form and that further precipitation occurred during the electrolysis.

Tucker and Schramm[226] stated that the addition of glycerine to the sulphate bath produced smoother deposits; this was also the experience of Vie[410] and of Klein.[17] Schlötter[222] also added glycerine to his electrolyte.

Ryss and Bogomolny[149] tested 24 addition agents, both organic and inorganic, and found none of value for improving the deposit. Watts and Li[319] investigated 43 addition agents; of these only ammonium oxalate and hexamethylenetetramine gave noticeably better deposits than were obtained in the absence of addition agents. Glue has been used in the commercial electrodeposition of iron to prevent treeing.

Patents relating to addition agents include the use of iron sulphocresylate in the chloride bath, by Cowper-Coles (British Patent 10,367, May 3, 1907), and the addition of boric acid, by Ottinger (German Patent 284,608, December 1, 1912). Ogawa and Horuichi (Japanese Patent 34,857, August 16, 1919) patented the addition of Japanese isinglass to the ferrous ammonium sulphate bath. Govaerts and Wenmaekers (German Patent 384,284, 1924) recommended the addition of an alkali thiosulphate and an organic acid to the sulphate bath.

It is generally acknowledged that the presence of organic substances in the electrolyte causes inclusion of carbonaceous matter in the deposit. Nicholson and Avery[73] found carbon present in deposits from an alkaline tartrate solution; with citric acid present in the electrolyte the amount of carbon in the deposit was larger. Avery and Dales[85,86] found 0.22 per cent of carbon in deposits from an ammonium oxalate solution and as much as 2 per cent of carbon in deposits from a citric acid solution. Verwer[106] in 1901 obtained similar results with deposits from an

oxalate solution. Frölich's work[557,609] indicated that the presence of organic compounds, either gases or salts, in the electrolyte may cause contamination of the deposit by carbon, the amount of contamination being less with ferrous chloride solution than with ferrous sulphate.

19. Summary of Data on Addition Agents.—A considerable number of addition agents, mainly organic compounds, have been tried in the electrodeposition of iron either to improve the operation of the bath or to improve the character of the deposit, or both. It is the consensus of opinion that addition agents are of little, if any, value in the electrodeposition of high-purity iron. In view of the conclusive evidence of contamination, the presence of organic material in the solution should be avoided where attainment of high purity in the deposit is desired.

D. ORGANIC ELECTROLYTES

A solution of ferric chloride in acetone was electrolyzed by Patten and Mott[197] in 1909. With a current density of 20 amp. per sq. dm. (186 amp. per sq. ft.) a deposit of iron was obtained, but with a lower current density, 6 amp. per sq. dm. (56 amp. per sq. ft.), the results were negative. Archibald and Piguet[361] reported that gray metallic iron free from carbon was deposited from solutions of ferric chloride in acetone and in acetone and water, provided the voltage was low. The same iron salt in a mixture of ethyl alcohol and acetone gave a deposit which contained carbon. Timmerman[150] found that a solution of ferric chloride in methyl chloride had good electric conductivity and upon electrolysis yielded metallic iron and chlorine.

Deposits of electrolytic iron were obtained from a solution of ferrous sulphate in a mixture of one part of acetone and two parts of water, according to Archibald and Piguet.[361]

Müller, Hönig, and Konetschnigg[525] electrolyzed a solution of ferrous bromide in pyridine (4.8 g. per liter) at 25°C. (75°F.) and obtained a crystalline deposit of iron.

The results obtained from attempts to deposit iron electrolytically from organic solvents, while possibly of scientific interest, have no apparent practical value.

E. FUSED ELECTROLYTES

A process of producing iron by electrolysis of a solution of iron oxide in molten calcium fluoride, with or without the

addition of carbon, was patented by Simon (British Patent 14,291, August 9, 1900; U. S. Patent 704,393, July 8, 1902). Beckman[229] described a process for obtaining metals from their ores by electrolyzing a fused bath composed of the metallic oxide and lime.

Crystalline iron was obtained by Aten, den Hertog, and Westenberg[594] by electrolysis of the fused chloride, using iron electrodes. A high current density, 15 amp. per sq. dm. (140 amp. per sq. ft.) was necessary. Sauerwald and Neuendorff[631] obtained 39.8 g. of iron by electrolyzing a fused bath composed of 75 per cent of purified iron oxide (25.1 per cent FeO, 74.6 per cent Fe_2O_3) and 25 per cent of silica for 30 min. with a current of from 25 to 50 amp. This bath melted at 1220°C. (2230°F.) and was a clear liquid at 1260°C. (2300°F.). The temperature maintained during the electrolysis was 1300°C. (2370°F.). In another experiment with a carbon anode and an iron cathode, 400 to 800 amp. were used at 10 to 13 volts, the electrodes being spaced 7 cm. apart. During the run of 3 hr., 258 g. of iron were obtained, the temperature being sufficiently low so that the iron was deposited in the solid state. A microscopic examination indicated the iron to be "quite pure" with only a trace of silica. The same workers[799] later reported further results with this process. In addition to the silicate baths, iron oxide that was fused without the addition of silica was used as an electrolyte. The iron obtained was stated to be carbon-free. Doubt has been expressed [229] whether the product of such processes should be regarded as the product of electrodeposition or of ordinary reduction by carbon at elevated temperatures.

The deposition of iron by electrolysis of fused electrolytes, as in the case of organic electrolytes, may be of interest but is not important. Iron produced in the presence of carbon at temperatures of 1000°C. (1830°F.) or more would hardly be expected to be of high purity.

F. AUTHORS' SUMMARY

The laboratory production of electrolytic iron is not particularly difficult. A number of baths are available but the preferred electrolytes are, in general, either of the chloride, sulphate, or mixed chloride sulphate types. Additions of other salts or compounds to the bath may improve the character of the deposit

or the operation of the bath, but are of questionable value if extreme purity of the product is desired. There is a wide range of optimum operating conditions, depending upon the type of bath and on the purpose of the process.

Electrolytic iron in general is of high purity, higher than that attained in iron or steel produced by smelting or by refining in the molten state. The total of the impurities determined in electrolytic iron seldom exceeds a few hundredths of 1 per cent but really pure iron, free from all impurities, has not been produced by electrodeposition even on a laboratory scale. The product invariably has been contaminated by elements which originated in the electrolyte, in the anode material, or in the substances added to the bath to improve its operation. Carbon, silicon, sulphur, and phosphorus usually were present and metallic elements such as copper, cobalt, and nickel sometimes were found. Hydrogen exists in greater or less amounts in all freshly deposited electrolytic iron, but this element can be removed readily and practically completely by a simple annealing treatment. The practice of reporting the purity of a sample of electrolytic iron as the difference between 100 per cent and the total of impurities determined is seldom justified by the completeness and accuracy of the analysis. The reported analyses, in general, do not justify more than a statement that the total of the fixed impurities determined, for that sample, did not exceed the observed amount.

The hope that electrolytic iron could be produced in such a pure state that its properties might constitute a radical improvement over the properties of commercial forms of iron has not been realized, as the discussion of the properties of electrolytic iron in the ensuing chapters will show. However, it should be noted that most of the attempts to prepare pure iron by electrolytic methods were made prior to 1920. Since that time there has been a constantly increasing appreciation of the fact that the first traces of an impurity, in amounts so small that they were formerly considered insignificant, may exert a profound influence on the properties of the metal. In recent years zinc, aluminum, and lead have been produced in states of purity previously not attainable, by means of electrolytic processes which were developed by careful, systematic consideration of all the details and variables involved. In each case the elimination of small amounts of impurities, previously considered insig-

nificant, resulted in a pronounced improvement in properties as compared with those of commercially pure metal. The possibilities of electrolytic purification of iron have not been investigated so thoroughly as was done for zinc, aluminum, and lead; in view of the results obtained with these three metals, it is possible that a painstaking, systematic investigation of such variables as the selection of an iron compound, the concentration of this compound in the electrolyte, the presence of added salts, the hydrogen ion concentration, the current density, and the temperature, might lead to production of iron of higher purity than was previously obtained. It should be possible to eliminate most of the impurities ordinarily present in electrolytic iron, although nickel and cobalt, if present in the anode material or in the electrolyte, might be difficult to remove.

COMMERCIAL PRODUCTION OF ELECTROLYTIC IRON

Commercial Refining Processes—Building-up Processes—Extraction Processes—Authors' Summary

In the commercial manufacture of electrolytic iron, extreme purity of the product is often of less importance than economy of operation or production of material with good structure. Hence, the conditions of deposition usually are different from those employed in the laboratory production of high-purity iron for scientific uses, as has been pointed out by Escard.[397] In spite of this sacrifice of extreme purity for the sake of expediency and structure, commercial electrolytic iron deserves to be classed as high-purity metal.

A. COMMERCIAL REFINING PROCESSES

The first commercial production of electrolytic iron is credited to Burgess and Hambuechen.[120] Their quantity production apparently was obtained under the same operating conditions that were described, in the preceding chapter, in the discussion of their laboratory experiments. This iron was considered to be extraordinarily pure but some recent comments* from the late Dr. John A. Mathews serve to emphasize the difficulties encountered in really determining the purity of high-purity iron. Dr. Mathews commented as follows:

Prof. Burgess first produced an electrolytic iron twenty-five years ago —and sent me a sufficient quantity to remelt in the crucible. The material was in the form of rough plates some $\frac{5}{8}$ to $\frac{3}{4}$ in. thick. On remelting and analyzing we were astonished to find the sulphur about 0.04 per cent. It was decided after some correspondence with Prof. Burgess that this was sulphur reduced from the iron sulphate electrolyte mechanically entrapped in the rather nodular deposit. Prof. Burgess had been determining the sulphur in his electrolytic iron by the evolution method and was reporting it extremely low, below 0.01 per cent. The

* Private communication.

sulphur in ferrous sulphate would not be liberated by the ordinary evolution method but was apparently reduced in the melting in the crucible, so that the resulting melt was very different from what Prof. Burgess thought his iron to be.

20. Production of Electrolytic Iron Printing Plates. Reference has been made previously to the earliest commercial application of electrolytic iron, as a supporting material for copper electrotype plates, and to the process proposed for that purpose by Klein.[17,21,31,39] Haber[79] stated that a similar process was in use at the Austrian Mint.

A recent development along this line is the process of Thomas and Blum[911] for preparing the electrolytic iron printing plates now used by the U. S. Bureau of Engraving and Printing. The bath, a modified Fischer-Langbein solution (see page 20), has a ferrous chloride concentration of about 3 N, and calcium chloride of 2 to 4 N. Free-acid concentration of about 0.01 N is maintained by hourly additions of hydrochloric acid. The pH of the bath is about 2, measured with a quinhydrone electrode. The bath is kept at about 90°C. (195°F.). The cell is a rubber-lined steel tank, with a thin inner lining of cypress to protect the rubber lining against impact or abrasion. Between the steel tank and a wooden tank surrounding it is a layer of cork or sawdust for thermal insulation. The anodes of ingot iron formerly were suspended in alundum pots but, according to a private communication, are now inclosed in asbestos bags. The anodes are removed every few hours and the sludge is brushed off. At the same time the electrolyte in the anode compartment is stirred, preferably by mechanical agitation as aeration of the bath causes oxidation of the iron salt and produces inclusions in the iron which reduce its ductility.

The negative plates or "altos" are soldered back to back, a thin coating of graphite is given each face, which is then coated with nickel to a thickness of about 0.4 mm. (0.015 in.). Iron is then deposited over the nickel to a thickness of about 5 mm. (0.2 in.). At 6.5 amp. per sq. dm. (60 amp. per sq. ft.) this requires about 84 hr. The nickel-faced iron "basso" plates are then stripped off, machined and ground to exact dimensions. The nickel face is finally plated with about 0.005 mm. (0.0002 in.) of chromium, to supply increased hardness to the printing surface.

The principal aim of Thomas and Blum's work was to produce electrolytic iron with satisfactory mechanical properties to serve as backing for printing surfaces of chromium-plated nickel. This aim was achieved. The structure of the deposit was fine-grained in the initial layers but consisted of coarse conical crystals in the later portions. As a result of this variation in structure, the plates as deposited, 5 mm. (0.2 in.) thick, could be bent around a cylinder with a radius of less than 20 cm. (8 in.) provided the face, that is, the surface first deposited, was on the convex side; but if the plate was bent in the opposite direction, it was more brittle.

In addition to the satisfactory mechanical properties, a high degree of purity of the product was obtained. Thomas and Blum reported that their electrolytic iron, after fusion in a magnesia crucible in an Arsem vacuum furnace, contained 0.013 per cent carbon, 0.005 per cent sulphur, 0.003 per cent silicon, 0.01 per cent nickel, and 0.02 per cent copper. Manganese and phosphorus were not detected. The total of the reported impurities was 0.051 per cent.

21. Cowper-Coles Process.—The process developed by Cowper-Coles[175] for the commercial production of sheets and tubes of electrolytic iron was covered by a number of patents granted in the period from 1906 to 1919. While the process did not meet with commercial success in England, the work of Cowper-Coles seems to have been the basis of the process operated successfully at Grenoble in France.

Cowper-Coles first specified a bath made by dissolving metallic iron in a solution of sulphocresylic acid. This bath seems to have been abandoned, however, as Palmaer and Brinell,[288] who investigated the Cowper-Coles process in 1913, stated that the electrolyte was a 40 per cent solution of ferrous chloride containing iron sulphocresylate as an addition agent, the amount present corresponding to 3 per cent of sulphocresylic acid. Iron oxide was added to the bath in the proportion of 300 g. per liter of electrolyte, making the bath a rather thick slurry. This served to polish the deposit on the rotating cathode, thus preventing gas pitting, and to prevent excessive acidity in the bath. The sulphocresylate bath was assumed to be at a temperature of 70°C. (160°F.); Palmaer and Brinell gave the working temperature of the chloride bath as between 88 and 95°C. (190 and 205°F.).

The cell used for the manufacture of tubes was a lead-lined trough with two cast-iron anodes laid on the bottom, the cross-section of the two anodes together being U-shaped. A cylindrical mandrel, rotating in the center of the U, served as the cathode. The mandrel was coated with lead which softened when heated, and thus facilitated the removal of the deposit. The lead coating also protected the mandrel from corrosion.

For the production of sheets of electrolytic iron a large cylindrical drum coated with an insulating material was suspended in the center of a cylindrical vat. The drum was rotated on its vertical axis and a removable metal sheet on the outer surface of the drum served as the cathode. The cast-iron anode bars were hung on the wall of the vat, but were insulated from it. The current density was from 6 to 8 amp. per sq. dm. (56 to 74 amp. per sq. ft.). Correct relation between speed of rotation and current density was essential to secure a satisfactory sheet or tube product in either of the types of cells.

According to Palmaer and Brinell, each ton of iron produced required: 1.1 tons of pig iron, 0.27 horse-power years of electricity for depositing, 0.05 horse-power year of electricity for machining, and about 50 man-hours of labor.

The product had excellent physical qualities but was not particularly pure, Cowper-Coles[175] giving the total impurities as from 0.132 to 0.193 per cent.

22. Bouchayer and Viallet Process. About 1908 Boucher acquired a license for the French rights to the Cowper-Coles process, which he then assigned to a holding company, Société "Le Fer." Numerous improvements were made in the original process and a license to manufacture tubes was granted Bouchayer and Viallet at Grenoble.[304,397,560] The right to manufacture sheets was secured by the St. Marie and Gravigny Foundry.

There is little mention in the literature of the manufacture of sheets of iron by this process, but the commercial manufacture of tubes seems to have been successful. An advantage is that thin tubes for radiators and boilers, the most expensive to manufacture by rolling, are the cheapest to make electrolytically. Production was stated by Belcher[546] in 1924 to have been 2 tons of tubes per day, with little labor or supervision necessary and with a high percentage of perfect tubes.

The cell used was similar in design to the Cowper-Coles cell. The mandrels on which the iron was deposited were 4 m. (13 ft.) in length and from 85 to 160 mm. (3.3 to 6.3 in.) in diameter. They were rotated at various speeds, according to the diameter, the 160-mm. mandrel making 180 to 200 r.p.m. The potential used was from 3 to 4 volts per cell. The cathodic current density decreased as the diameter of the mandrel increased, the same amperage being used for all cells regardless of the size of the mandrel. The correct relation between current density and peripheral speed was maintained by variation in the speed of rotation of the different-sized mandrels.

The electrolyte was a concentrated ferrous chloride solution heated electrically by means of an alternating current supplied through graphite electrodes. The working temperature of the bath was 70 to 75°C. (160 to 165°F.). Rapid circulation of the electrolyte was obtained by the use of pumps which passed the solution through vats filled with iron turnings. This insured neutrality and also filtered out insoluble impurities. Oxychloride of iron, which acted as a depolarizer to prevent the liberation of hydrogen, was formed by the use of an auxiliary anode of graphite.

After the deposit had reached the required thickness of 2 to 5 mm. (0.08 to 0.2 in.), the mandrel was removed from the cell, washed, and placed in a slow-speed lathe where a traveling gas jet heated the tube sufficiently to make it ductile. It was then rolled to expand the metal and to loosen it from the mandrel. After removal from the mandrel the tube was given a thorough anneal. As in the Cowper-Coles process the mandrel was first polished and then lead coated in a lead perchlorate bath.

Analyses[304,500,546] of the electrolytic iron produced by Bouchayer and Viallet, which was given the trade name "Beve" iron, showed total impurities to be between 0.025 and 0.043 per cent. However, the analyses did not include lead or copper and, as Bouchayer stated that the former was present to the extent of from 0.02 to 0.20 per cent and the latter from 0.02 to 0.10 per cent, the iron content of the material was undoubtedly less than the analyses indicated. The susceptibility to rusting, which is usually an important feature in iron deposited from chloride baths, apparently was overcome in this iron by the annealing

treatment immediately after deposition at temperatures high enough to volatilize chlorides present in or on the iron.

The Niagara Electrolytic Iron Company started the manufacture of electrolytic iron tubes and sheets at Niagara Falls about 1925, using the Boucher process. The plant and process have been described in two anonymous articles[592,593] and by Kreutzberg[616] and Boylston.[766] The properties of the product were given by Fuller.[662] It is understood that production was discontinued for economic reasons.

The production of tubes of electrolytic iron on a rotating mandrel which served as cathode in the electrolysis also was started at Cheshire, England,[567] but details of the process and of the production attained are lacking. The determination of an unusual number of the properties, thermal, electric, magnetic, and mechanical, of the product was reported, including the following analysis: 0.031 per cent carbon, 0.02 per cent manganese, traces of silicon, sulphur, and phosphorus; copper and nickel absent.

23. Western Electric Company Process.—In 1915 the Western Electric Company began production of electrolytic iron for magnet cores, the brittleness of the product allowing it to be readily pulverized to the fineness necessary for that purpose. Details of the process have been supplied by Storey,[357] McMahon,[479] Stoughton,[491] and Skowronski.[582]

The electrolyte used was that proposed by Watts and Li, a solution of ferrous sulphate, ferrous chloride, ammonium sulphate, and ammonium oxalate. A small quantity of glue was added to lessen treeing. The anodes were bars of openhearth steel, the cathodes were polished steel plates. The bath was operated at room temperature with a current density of about 1.3 amp. per sq. dm. (12 amp. per sq. ft.). When the deposit reached a thickness of about $\frac{1}{4}$ in., each alternate cathode was removed and stripped, and replaced by a fresh cathode. This avoided the extreme change in conditions that would occur if a complete set of new cathodes were installed all at once.

The product, after being washed and dried, was crushed, sieved, coated with zinc by tumbling with zinc dust, lightly shellacked, and compressed under a pressure of 200,000 lb. per sq. in.

Storey[357] stated that the production in 1916 was 1000 lb. weekly. Skowronski,[582] who reported the purity of the product as 99.97 per cent, stated that the production in 1925 was 25,000 lb. weekly. This production of electrolytic iron was discontinued when the material was supplanted by permalloy for use as magnet cores.

24. Langbein-Pfanhauser Process.—The Langbein-Pfanhauser Werke began producing electrolytic iron about 1909, using the ferrous chloride calcium chloride bath developed by Fischer. Engelhardt[396] stated that the scarcity of copper during the World War led to expansion of the Langbein-Pfanhauser plant and to the erection of an electrolytic iron plant by Siemens-Halske, the combined production being 400 tons per month. The softness of the annealed electrolytic iron made it an acceptable substitute for copper for certain purposes, such as shell bands. Engelhardt stated that for economic reasons the production of electrolytic iron in Germany was discontinued at the close of the World War.

The Langbein-Pfanhauser operation was described briefly in two anonymous articles[188,344] and in considerable detail by Pfanhauser.[935] The cells were composed of concrete with an acid-proof lining. Porous cups surrounded the cathodes. The bath, kept between 80 and 90°C. (175 and 195°F.) by steam heat, was electrolyzed with a current density averaging 3 amp. per sq. dm. (28 amp. per sq. ft.) although as high as 6.4 amp. per sq. dm. (60 amp. per sq. ft.) could be used. The average current efficiency was 94 per cent. The purity of the product is indicated in Table 5. These analyses are presumably of material produced on a laboratory scale in the development of more extensive operations. Pfanhauser[935] gave the cost of production, including interest and amortization, as 160 Reichsmarks per 100 kg. of electrolytic iron. This was equivalent to $350 per ton of iron.

A ferrous chloride potassium chloride electrolyte was used by Siemens-Halske. Otherwise their method of deposition, as described by Pfanhauser,[935] was similar to that of Langbein-Pfanhauser.

25. Present Status of Commercial Production of Electrolytic Iron in the United States.—Information has recently been

received* that the National Radiator Corporation, of Johnstown, Pennsylvania is prepared to furnish electrolytic iron in commercial quantities, in sheet or powder form. Details of the process are not available. The iron is said to contain 0.004 per cent carbon, 0.002 per cent manganese, 0.002 per cent silicon, 0.004 per cent phosphorus, 0.001 per cent sulphur; copper, nickel, chromium, and titanium, "unable to identify." Prices from 35 cents to $1 per lb. have been quoted, depending upon the sizes and quantities ordered. So far as the authors are aware, this is the only current production of electrolytic iron on a commercial scale in this country.

26. Summary of Electrolytic Iron Production by Commercial Refining Processes.—The production of electrolytic iron in quantity has been achieved in several commercial refining processes. A variety of baths have been used, with a general preference for the chloride bath or one of its modifications on account of the rapid deposition of iron obtainable from this type of bath. Typical analyses, listed in Table 5, indicate that electrolytic iron that is produced in quantity is a product of high purity, even though some of the purity obtainable in small-scale operations has been sacrificed to operating expediency. The commercial production of electrolytic iron usually has been undertaken either as an emergency measure or to supply metal with unusual properties or for unusual purposes. Operations in general have been short-lived for economic reasons. So far as is known, there is at present only one producer of electrolytic iron as a market commodity, in the United States.

B. BUILDING-UP PROCESSES

27. Electrodeposition of Iron for Building Up Machine Parts.—The use of electrodeposition of iron for "building up" worn or undersized parts of machinery was developed in England during the World War although Storey[357] stated that Krupp patented this application of the electrodeposition of iron in 1900. Mac-Fadyen,[406] Thomas,[423] Barclay,[426] Hughes,[436,473] and McLare[572] have given information on the British practice. McLare stated that a concentrated ferrous ammonium sulphate solution containing from 3 to 3.75 lb. of the salt per gal. (360 to 450 g. per liter) was used at room temperature. The solution

* Private communication, October 27, 1934.

TABLE 5.—ANALYSES OF ELECTROLYTIC IRON FROM OPERATIONS DESIGNED FOR QUANTITY PRODUCTION

Types of electrolyte	Process	Reference	Composition, per cent							Total of fixed impurities determined
			C	S	P	Mn	Si	Cu	Other impurities	
Ferrous sulphocresylate	Cowper-Coles	175	0.060	0.016	0.041	Trace	0.011	......	0.004 As	0.132
Chloride with sulphocresylate	Cowper-Coles	288	0.08	0.02	0.042	0.05	0.009	......	0.18 Cl, 0.021 H	0.201
Chloride	Bouchayer and Viallet	304	0.004	0.006	0.008	......	0.007	......	....	0.025
Chloride	Bouchayer and Viallet	500	0.029	0.0048	0.0037	......	0.004	0.02 to 0.10	0.02 to 0.20 Pb	.....
Chloride	Bouchayer and Viallet	397	0.008	Trace	0.002	0.009	0.014	......	....	0.033
Chloride	Langbein-Pfanhauser	349	0.008	0.004	Trace	Trace	0.006	0.011	....	0.029
Chloride	Niagara Electrolytic Iron Co.	592	0.004	0.006	0.003	0.000	0.004	0.017	No Ni or Pb	0.034
Chloride	Niagara Electrolytic Iron Co.	662,766	0.006	0.004	0.005	0.000	0.005	0.015	....	0.035
Chloride	Fischer-Langbein	911	0.013	0.005	Nil	Nil	0.003	0.02	0.01 Ni	0.051
Sulphate-chloride	Westinghouse Co.	385A	0.010	0.003	0.003	Trace	0.004	Trace	0.009 Al	0.029
Sulphate-chloride	Western Electric Co.	479	0.014	0.003	0.013	0.029	0.028	......	....	0.087
Sulphate	Plant at Cheshire, England	567	0.031	Trace	Trace	0.002	Trace	Nil	No Ni	0.051

was kept neutral or very slightly acid.   The use of a large vat
facilitated control of the acidity and eliminated the need for
continual agitation, only an occasional stirring then being
necessary.   Where small baths were required, as when the
containing vessel had to be built around the work, careful control
of concentration and acidity was necessary.   With large vats a
current density of 1.9 to 2.2 amp. per sq. dm. (18 to 20 amp.
per sq. ft.) was used; with small baths the density was about
1.6 amp. per sq. dm. (15 amp. per sq. ft.).   When deposition
was continued without attendance, for example over night, the
current density was cut to about 1.3 amp. per sq. dm. (12 amp.
per sq. ft.).   Deposition was carried on continuously to comple-
tion; interruptions in deposition produced poorly adherent layers
of metal.   The temperature of the bath was not allowed to drop
below 18°C. (65°F.), as deposition at lower temperatures pro-
duced poor deposits.   The anodes of soft Swedish iron entirely
surrounded the cathode and had an area at least four times that
of the cathode.   The anodes were removed periodically and
scrubbed.   Water lost from the bath by evaporation was replaced
with distilled water.

The Westinghouse Electric and Manufacturing Company used
a similar process for the same purpose.   The latest information
(1930) on the Westinghouse method* is given by Thomas.[865,949]
Earlier writers who described the American practice are Alley[494]
and Kellogg.[476]   The electrolyte used by Westinghouse was a
rather concentrated ferrous ammonium sulphate solution,
300 g. per liter (2.5 lb. per gal.), to which was added a small
amount of freshly precipitated ferrous carbonate to preserve
neutrality, and a small amount of charcoal to prevent gas pitting.
The bath was kept at 60°C. (140°F.).   At the current density
used, 6.5 to 7 amp. per sq. dm. (60 to 65 amp. per sq. ft.), 0.006 in.
was deposited per hr.   Stoneware tanks were used for small work,
and lead-lined wooden tanks for large pieces.   Unlined wooden
tanks could not be used as the organic material extracted by the
electrolyte caused pitting.   The anodes were round bars of ingot

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* Since this manuscript was prepared, Kellogg[1079] has published an addi-
tional account of the building-up operations at the Westinghouse Electric
and Manufacturing Company.   Details of the process are essentially as
given by Thomas in the ensuing text.   It has been found that an adherent
deposit of electrolytic iron can be obtained on cast iron.

iron with a micarta disk fastened to each end. An up-and-down motion was imparted to the anodes by the rocker arm from which they were suspended, causing agitation of the electrolyte which was essential to the production of satisfactory deposits. The pieces which were to be built up were suspended near the anodes through holes in the micarta disks. Parts of the cathode not to be plated were covered with an insulating wax mixture. Good adherence could be obtained only if the articles were carefully cleaned. In addition to cleaning with organic solvents and caustic soda to remove grease, they were cleaned electrolytically in a 30 per cent sulphuric acid solution, using a current density sufficiently high, 46.5 amp. per sq. dm. (3 amp. per sq. in.), to cause the iron to be passive.

C. EXTRACTION PROCESSES

The idea of preparing electrolytic iron directly from the ore, in place of refining iron produced by a smelting operation, seems to have originated with Siemens, who was granted a patent (U. S. Patent 415,576) for such a process in 1889. It described the treatment of a sulphide ore with a ferric salt solution, either sulphate or chloride, which dissolved the ore with the formation of ferrous salts and free sulphur, as indicated by the equation:

$$2FeCl_3 + FeS = 3FeCl_2 + S$$
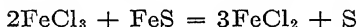
When the ferrous salt solution was electrolyzed in a two-compartment cell with insoluble anodes, iron was deposited at the cathode and ferric salts were formed at the anode. The ferric salt solution was used to dissolve more ore, completing the cycle of operations. These reactions were the basis of several later processes of iron extraction and deposition.

28. Eustis Process.—The essential reactions of the process developed on a pilot-plant scale at Milford, Connecticut, by Eustis, Perin, and Belcher[445,466,519,546] are the same as those of the Siemens process. The pilot plant was designed to produce 1 ton of electrolytic iron per day, but no production records have been found in the literature.

A countercurrent system was used to obtain solution of the maximum amount of iron from the ore, a Canadian pyrrhotite, and at the same time to obtain complete reduction of the ferric iron present in the used electrolyte. The completely reduced

solution from the treatment of the ore was pumped to cementation tanks where the copper was precipitated with scrap iron and recovered. Calcium sulphide was then added to the solution, causing precipitation of the metallic impurities with the exception of zinc. No satisfactory treatment was found for eliminating zinc; the deposit of electrolytic iron contained about 0.02 per cent of this element. It was planned to recover sulphur from the residue remaining after treatment of the ore.

The purified ferrous chloride solution was pumped to storage tanks whence it was circulated through the cell at such a rate that the ferric iron content of the anolyte never exceeded 72 g. per liter. This prevented evolution of chlorine at the anode.

As the calcium and magnesium carbonates and the zinc sulphide present in the ore dissolved more readily than did the iron sulphide, their solution represented a continual loss of effective chlorine. To prevent this loss the ore was given a preliminary wash with a very dilute sulphuric acid solution, which rid the ore of the carbonates and zinc sulphide without appreciably attacking the iron sulphide. Pyrite ore could be used in the process, provided the pyrite was given a preliminary roast in a reducing atmosphere to drive off part of the sulphur and to form an artificial pyrrhotite.

The cell first used was similar to that used by Bouchayer and Viallet, with a revolving mandrel as a cathode. The driving mechanism and electric connections gave trouble so this type of cell was abandoned. Cells with stationary cathodes were tried but were unsuccessful, the deposits being too rough to permit rolling to sheets.

The cell finally adopted was equipped with a rotating mandrel cathode, but with the driving mechanism, stuffing boxes, and electric connections of improved design. A peripheral speed of 250 ft. per min. permitted use of a current density of 11 amp. per sq. dm. (100 amp. per sq. ft.) with the electrolyte above 70°C. (160°F.) and preferably just below boiling. Successful operation on an experimental scale was attained with electrolytes containing between 75 and 275 g. of iron per liter, but a concentration of 180 g. of iron per liter was recommended.

Iron produced in the Milford plant was stated[546] to contain a total of 0.037 per cent of fixed impurities, distributed as follows: 0.03 per cent carbon, 0.002 per cent silicon, 0.003 per cent

sulphur, 0.002 per cent phosphorus; manganese absent. The sulphur content of the product was satisfactorily low, particularly

REACTIONS

Agitators
$FeS + 2FeCl_3 = 3FeCl_2 + S$
$RS + 2FeCl_3 = 2FeCl_2 + RCl_2 + S$
$\quad R$ being $Cu, Pb, Zn,$ etc.

Cementation
$CuCl_2 + Fe = FeCl_2 + Cu$
$PbCl_2 + Fe = FeCl_2 + Pb$

Electrolysis
$3FeCl_2 \longrightarrow Fe + 2FeCl_3$
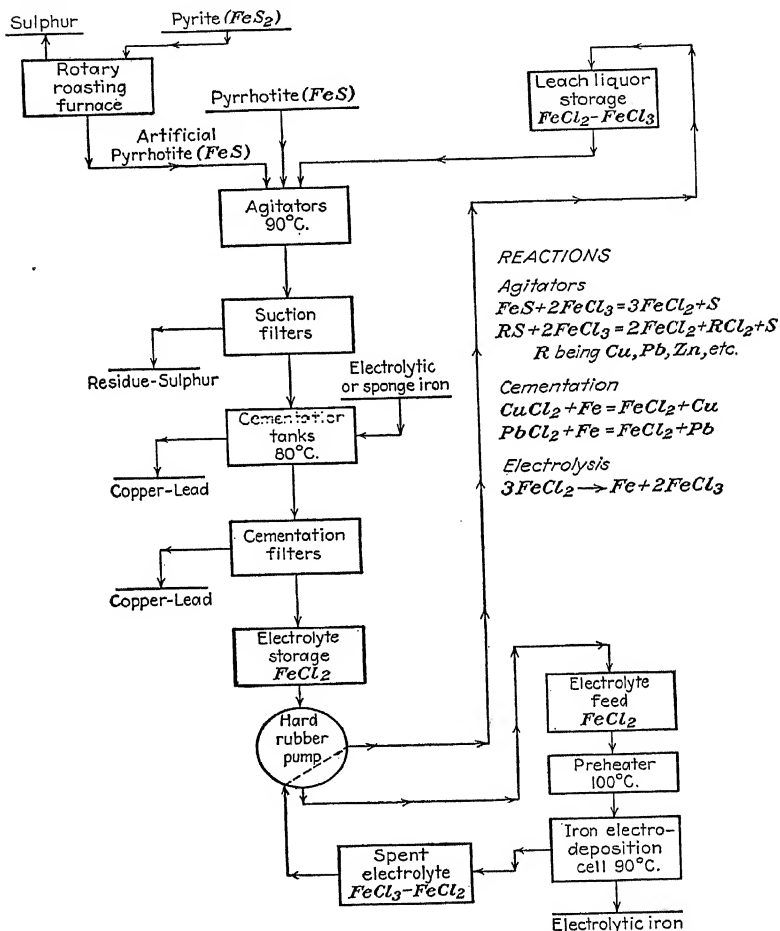
FIG. 3.—Flow sheet of the Traill and McClelland[584] process for the production of electrolytic iron from pyrrhotite ores.

in view of the fact that the starting point of the process was a sulphur-rich ore.

29. Traill and McClelland Process.—An extraction process
for production of electrolytic iron was developed by Traill,
McClelland, and co-workers[534,535,584,621,635,692] at the Hydro-
metallurgical Laboratory of the Canadian Department of Mines,
with a view to the utilization of Canadian pyrrhotite ores.   The
process, as far as chemical reactions are concerned, is the same as
that of Eustis and is shown in the flow sheet, Fig. 3.   As artificial
pyrrhotite, produced by roasting pyrite in a reducing atmosphere,
dissolved more rapidly than did the natural pyrrhotite ore and
did not require such fine grinding, it was mixed with the natural
ore prior to leaching.

A rotating mandrel cathode was used in most of Traill's work,
although a cell with a stationary cathode and rapid circulation
of the electrolyte around the cathode was also tried.   The latter
cell avoided the difficulties with driving mechanism, stuffing
boxes, and electric connections inherent in the former type.
In both cells the temperature was 80 to 90°C. (175 to 195°F.), cell
voltage 4 to 4.4, pH 3.7 to 3.9, and iron content in the electrolyte
170 to 185 g. per liter.   A current density of 11 amp. per sq.
dm. (100 amp. per sq. ft.) was used with the rotating cathode, and
3.8 amp. per sq. dm. (35 amp. per sq. ft.) with the stationary
cathode.

Chalcopyrite concentrates were also tried in this process but,
although the copper leached readily, only half of the iron would
dissolve.   A preliminary reducing roast converted all of the iron
to the soluble form.   A better procedure was to leach the raw
concentrates, roast the residue with recovery of the sulphur,
and add the roasted residue to the next batch of raw concentrates.
As much as 98 per cent of the iron, 98.8 per cent of the copper,
and 60 per cent of the sulphur could be recovered.

A process for the utilization of the ilmenite ores of Canada
with recovery of electrolytic iron and titanium oxide was also
developed by Traill and McClelland.[636,679,691,866]   The finely
ground ore was reduced with carbon at 1000°C. (1830°F.),
giving a product which contained about 44 per cent of metallic
iron and leaving the titanium oxide unattacked.   The product
was leached with anolyte liquor which dissolved the metallic
iron with reduction of the ferric iron of the solution.   The residue
after leaching contained 76.2 per cent of titanium oxide and
3.7 per cent of iron.   This residue was treated for the recovery

of pure titanium oxide for use as a pigment. The ferrous chloride solution was electrolyzed for the recovery of iron.

30. Pike Process.—The process developed by Pike[901] had as its primary object the recovery of copper from chalcopyrite concentrates, the electrolytic iron recovered in the process being a by-product of secondary importance.

The complicated nature of these electrolytic extraction processes is illustrated by the flow sheet for Pike's process,

Fig. 4.—Flow sheet of the Pike process for the production of electrolytic iron as a by-product of the recovery of copper from chalcopyrite ores. (*Pike, West, Steck, Cummings, and Little.*[901])

Fig. 4. The ore was leached in tank 1*a* with hot iron chloride solution containing about 100 g. of iron per liter, of which about half was in the ferric state. To obtain high copper extraction an excess of leaching solution was used. This resulted in only partial reduction of the ferric iron; the reduction was completed with pyrrhotite ore in tank 1*b*. The tailings were filtered in 2 and treated in 17 to recover their sulphur; the residue from 17 was roasted in 18, under such conditions that the sulphate needed in the process was formed. The roasted tailings were then leached with some of the anode electrolyte in tank 15.

The final tailings, which were filtered in 16, contained all of the gold of the ore. The leach liquor, containing sulphate which must be removed later in the process, was used for treating ore in tank 1a. The liquor from 2 was passed over copper in 3a, 3b, and 3c to cement out the silver. Copper was cemented out on scrap or sponge iron in 4a and 4b; the settled sludge was filtered out in 5. The decanted solution passed through tower 6, where H_2S was introduced to remove traces of copper and any zinc present. After filtration in 7, the solution passed through disk evaporator 8 where the water, which was condensed from the steam injected to heat the solution, was removed. The solution now contained about 12 per cent of ferrous iron and only traces of ferric iron. In correction tanks 9a and 9b sufficient sulphuric acid was added to bring the pH to 2.5, and sufficient calcium chloride to restore the chlorine lost in the process, the equivalent calcium being precipitated by the sulphate which entered the cycle with the leach liquor from 16. After filtration in 10, the solution was pumped to storage tank 11, which fed electrolytic cell 12. The anode electrolyte drained to 13, whence it was pumped to leaching tank 1a. The cathode electrolyte was circulated by draining it to 14, and pumping it back to 11.

The electrolytic cell, designed for this process, had revolving disk cathodes, woven asbestos cloth diaphragms, and graphite anodes. The cathodes were slightly less than half submerged, and the exposed portion was covered with a hood of cork board which protected the deposit from chilling. The cathodes were prepared before deposition by heating them to form a coating of blue oxide, which facilitated stripping. Cells with stationary cathodes were not satisfactory as the snags caused by excessive treeing tore the diaphragms when the cathodes were removed from the cell. Rubbing the cathode during deposition was found to be unnecessary; it improved the deposit somewhat but not enough to justify the expense. Operating conditions were: current density 3.8 to 5.5 amp. per sq. dm. (35 to 50 amp. per sq. ft.), temperature of the catholyte above 80°C. (175°F.), temperature of the anolyte 90 to 95°C. (195 to 205°F.), ferric iron in the catholyte never over 0.05 per cent, pH 2.5.

In pilot-plant operation Pike's process produced about 3000 lb. of electrolytic iron. The average composition of this material was reported[901] to be 0.005 per cent carbon, 0.007 per cent

sulphur, 0.006 per cent copper, with phosphorus, silicon, manganese, nickel, cobalt, cadmium, arsenic, zinc, and lead absent. Several samples contained as little as 0.003 per cent sulphur and 0.004 per cent copper, leading Pike to believe that these limits could be held in regular operation. The analyses are unusually complete and permit a definite statement that the average value for the total of fixed impurities in this material did not exceed 0.018 per cent.

31. Kangro Process.—The process devised by Kangro for the production of electrolytic iron from iron ores was described by Pfanhauser.[935] The basis of the process was the discovery by Kangro and Flügge[836] that chlorine reacted with iron oxide at 800 to 1000°C. (1470 to 1830°F.) to form ferric chloride which distilled from the gangue and was obtained comparatively pure. The aqueous solution of the ferric chloride was then electrolyzed in two stages, using insoluble anodes. In the first stage the ferric chloride was reduced to ferrous chloride; this was then electrolyzed to produce electrolytic iron.

32. Estelle Processes.—Two processes for the preparation of electrolytic iron from iron ores were devised by Estelle.[465] The process patented by him in 1914 was a modification of the Siemens process. Sulphide iron ore, either natural pyrrhotite or an artificial pyrrhotite made by roasting pyrites in a non-oxidizing atmosphere, was treated with hydrochloric acid. The hydrogen sulphide which was evolved was recovered for later use in the process. The ferrous chloride solution formed was treated with iron to remove copper and was then electrolyzed in a simple cell, using an insoluble anode. Iron deposited on the cathode and ferric ions were formed at the anode. When the concentration of ferric iron was sufficiently high the cell liquor was passed through a tower where it reacted with hydrogen sulphide from the leaching operation, with reduction of the ferric iron to the ferrous state, the liberation of sulphur, and the formation of free acid. The sulphur was recovered as a by-product. The solution, which now contained ferrous iron and free acid, was used to leach fresh ore.

To avoid the difficulties encountered in handling hot ferric chloride solution, Estelle later developed the process usually associated with his name. Ores of the oxide type such as hematite, limonite, magnetite, and "blue billy" (the roasted

pyrite cinder from sulphuric acid plants) are most suitable for this process. Sulphide ores require a preliminary treatment which involves the use of sulphuric acid and ammonia to convert the iron to the hydroxide in which form it was added to the electrolytic cell (U. S. Patent 1,565,353, December 15, 1925; Canadian Patent 262,090, June 29, 1926). The cost of this treatment makes it doubtful whether the Estelle process can be operated successfully on a commercial scale with sulphide ores.

Oxide ores, however, require only heating with caustic soda or soda ash and hydrolysis of the ferrite formed to convert the iron to the hydroxide, which is comparatively pure, as most of the impurities dissolve in the caustic soda. After filtration the caustic soda is regenerated by diluting to 20 per cent, adding milk of lime, filtering, and concentrating.

The cell used by Estelle was an iron tank which also served as the anode; the cathodes were iron plates. The electrolyte was prepared by adding 30 parts of the hydrated iron to 70 parts of a 50 per cent caustic soda solution. Estelle specified 20 amp. per sq. dm. (186 amp. per sq. ft.) as the correct current density. Lloyd[842] found 90°C. (195°F.) the most suitable temperature for electrolysis. Iron hydroxide was continually added to replace that reduced at the cathode. The electrolyte was regenerated when necessary in the same manner as was the caustic soda used in treating the ore. With an air-tight cover on the cell, the oxygen evolved at the anode could be collected and sold as a by-product. No complete analyses of iron from this process are available. Lloyd found 0.004 and 0.005 per cent phosphorus and 0.002 and 0.053 per cent sulphur in two samples which he prepared. The Estelle process has never been exploited commercially although Lloyd, who made a laboratory study of the process, believed it worthy of investigation on a larger scale.

33. Other Processes.—A process of reducing iron oxide by making it the cathode in an alkaline electrolyte containing a soluble sulphide was patented by Rodman (U. S. Patent 884,763, April 14, 1908). Ramage in 1910 patented a process for recovering iron from its ores by reducing the ore to sponge iron, which was compacted and used as the anode in an electrolytic bath (U. S. Patent 949,004, February 15, 1910). Parker patented a similar process in 1890 (British Patent 9991, June 27, 1890).

Patents to Ramage (U. S. Patents 984,703 and 1,007,388) in 1911 covered a process of dissolving iron oxide in sulphuric acid, reducing with sulphur dioxide, and electrolyzing with sulphur dioxide as a depolarizer. The sulphuric acid formed was used to treat more iron oxide.

Numerous patents were granted to Dekker* covering processes of converting iron ores to iron sulphate, which was then electrolyzed. Molten $FeSO_4.7H_2O$ was used as electrolyte in the cathode compartment. The anode compartment was packed with iron compounds, obtained by hydrolysis of iron salts, which dissolved in the sulphuric acid formed at the anode.

Farnham in 1912 patented a process in which sulphuric acid, obtained by the electrolysis of ferrous sulphate, could be used to form more ferrous sulphate (U. S. Patent 1,006,836, October 24, 1912). In the following year, a patent was granted to Reed (U. S. Patent 1,055,652, March 11, 1913) which specified the use of a lead anode in electrolyzing ferrous sulphate, the sulphated lead being then used as a cathode in a second electrolysis for the recovery of the sulphuric acid.

Pip electrolyzed a ferrous salt solution, using the ferric solution formed at the insoluble anode to dissolve spathic iron ore (German Patent 316,597, June 26, 1918).

Conder[504] proposed the treatment of pyrites in a suitable furnace with hydrogen, passing the evolved hydrogen sulphide into a ferric chloride solution to form ferrous chloride, free hydrochloric acid, and sulphur. The sulphur was recovered and the acid ferrous chloride solution was used to dissolve the iron sulphide formed in the hydrogen treatment. After removal of any copper present, the ferrous chloride solution was

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* British Patent 18,488, August 16, 1911.
  German Patent 268,142, August 17, 1911.
  French Patent 445,758, July 4, 1912.
  Swiss Patent 67,394, July 18, 1912.
  British Patent 28,857, December 14, 1912.
  German Patent 273,046, February 14, 1913.
  U. S. Patent 1,075,409, October 14, 1913.
  U. S. Patent 1,113,546, October 13, 1914.
  Norwegian Patent 27,816, April 10, 1917.
  British Patent 117,638, April 21, 1917.
  Swiss Patent 76,764, February 1, 1918.
  Canadian Patent 192,268, August 19, 1919.

electrolyzed, with deposition of iron and formation of more ferric salts, which were treated with hydrogen sulphide. Conder's process is similar to Estelle's first process.

In the process proposed by Okochi and Hanoaki, easily crushable iron ores are reduced to metallic iron, mixed with iron sulphide, and used as anode in an acid electrolytic bath (U. S. Patent 1,582,423, April 27, 1926).

34. Summary of Extraction Processes for the Production of Electrolytic Iron.—Extraction processes for the production of electrolytic iron directly from ores have been successful from a technical but so far not from an economic point of view. Iron of satisfactory purity and properties has been produced on an experimental scale, but lack of a market for electrolytic iron and the cost of the process have not warranted continuous operation.

Most of the processes were designed for the production, in addition to electrolytic iron, of valuable by-products both metallic (such as copper, silver, and gold) and non-metallic (sulphur or titanium oxide). The handling of the hot, corrosive solutions of ferrous and ferric chloride employed in most of the extraction processes is difficult even in small-scale operations and creates an extremely difficult problem in plant design and in the selection of materials of construction for operation on a larger scale.

D. AUTHORS' SUMMARY

Electrolytic iron has been produced in several instances on a scale of operations decidedly greater than that of laboratory production. In quantity production there was generally a slight sacrifice of purity of the product for the sake of increased efficiency of operation; nevertheless the product should be rated as a metal of high purity. The chloride bath was usually preferred, on account of the high current densities and consequent rapid deposition obtainable in this type of bath. The commercial production of electrolytic iron usually was undertaken as an emergency measure or to produce material with special properties for particular uses, but even in the special uses electrolytic iron usually has been supplemented by cheaper material with equally desirable properties. Consequently, most of the operations for commercial production of electrolytic iron have been technical

but not financial successes and have been short-lived. For general use the properties of electrolytic iron are not so much superior to those of ordinary iron as to justify the increased cost of the electrolytic product. However, as was stated in the summary of Chapter I, the authors are not convinced that the possibilities of producing very pure iron by electrolytic methods have been exhausted. There is still a possibility that improved processes may yield electrolytic iron of higher purity than has been attained to date. The properties of this very pure iron remain to be determined.

Several processes have been proposed for the production of electrolytic iron directly from ores. Most of these processes were designed to treat sulphide ores so as to produce a solution of ferrous chloride from which electrolytic iron could be recovered; a few processes have been proposed for the treatment of oxide ores. Frequently the hope has been entertained that valuable by-products, either metallic or non-metallic, would help to defray expenses, but the lack of demand for electrolytic iron in quantity and the cost of operation have prevented attempts to operate extraction processes on anything but an experimental, or, at most, a pilot-plant scale.

CHAPTER III

CHEMICAL METHODS FOR PREPARING HIGH-PURITY IRON

Reduction Methods—Thermal Decomposition of Iron Carbonyl—Melting or Compacting—Preparation of Single Crystals—Authors' Summary

For the preparation of high-purity iron for scientific uses, electrolytic methods have been preferred by most workers. However, for atomic weight determinations, where extreme purity is essential to accuracy, chemical methods have been used. Furthermore, chemical methods are of industrial importance as the production of commercially pure iron in large quantities is accomplished by reduction and refining, *i.e.*, by chemical methods of purification.

A. REDUCTION METHODS

Volger[29] stated that probably the first instance of the preparation of high-purity iron, by reduction methods, was that of Peligot[3] in 1844, who reduced iron chloride with hydrogen and obtained octahedral crystals of iron which were made into small malleable plates. DeLuca[13] in 1860 precipitated ferric hydroxide from ferric chloride solution with ammonia. The precipitate was filtered, ignited, and reduced with hydrogen. Emphasis was placed on the necessity for careful purification of the hydrogen. Contamination by sulphur was encountered unless all of the rubber tubing used was previously boiled in potassium hydroxide solution.

35. Reduction with Hydrogen.—Probably the first serious attempt to prepare pure iron by hydrogen reduction was that of Matthiessen and Szczepanowski[18,22] in 1868–1869. Their work, which was sponsored by the British Association for the Advancement of Science, was the initial step in an investigation of the "chemical nature of cast iron." The plan was to prepare

pure iron, determine its properties, then to add singly the various elements contained in cast iron and thus determine the effect of each element upon the properties of the iron.

Matthiessen and Szczepanowski used four general methods in their attempts to prepare pure iron:

1. Ferrous oxalate was precipitated, ignited, and reduced with hydrogen. Even with two precipitations as oxalate, the product contained sulphur.

2. Ferric chloride was purified by sublimation, dissolved in water, and the hydroxide precipitated with ammonia. After filtering, washing, igniting, and reducing with hydrogen, the iron contained sulphur.

3. Ferrous sulphate was fused with sodium sulphate. The resulting iron oxide was washed, ignited, and reduced with hydrogen. The iron contained sulphur. Replacement of the sodium sulphate with sodium chloride resulted in contamination with platinum from the crucible used for the fusion.

4. Iron obtained by the above processes was treated with oxygen, steam, nitric acid, and mixed ammonia and oxygen, followed by hydrogen reduction. The iron was still contaminated with sulphur.

The third method was finally selected as giving the purest material and a considerable quantity of iron was prepared as follows: The purest ferrous sulphate obtainable was dissolved in water, the solution acidified with acetic acid, and hydrogen sulphide passed in to precipitate the heavy metals. After filtration the ferrous sulphate was twice recrystallized and then dried, first on a water bath and then on an air bath. Sodium sulphate was recrystallized several times to eliminate sodium chloride, which caused contamination by platinum. The crystals were then melted on the steam bath whereupon anhydrous sodium sulphate separated. The purified ferrous sulphate and sodium sulphate were mixed and fused in platinum. The melt, after cooling, was leached with boiling water. The combined product from six or eight fusions was washed by decantation until no sulphates could be detected in the wash water; the iron oxide was then ignited and reduced with hydrogen in a platinum crucible. The hydrogen, prepared by the action of sulphuric acid on zinc, was purified by passing through silver nitrate solution, lead acetate solution and over caustic soda. The spongy iron resulting from the reaction was compacted by

means of a diamond mortar and a copying press. The resulting buttons were melted on lime, by means of an oxyhydrogen flame. After melting, the oxygen was shut off and the melt cooled in hydrogen. The investigators stated[22] that the product was free from phosphorus, silicon, and calcium; the sulphur content was reported by one analyst as 0.0007 per cent, by another as 0.00025 per cent.

Methods involving the precipitation of ferrous oxalate as a means of preparing a pure salt of iron have been rather extensively investigated. Dragendorff[24] in 1872 precipitated ferrous oxalate by addition of potassium oxalate to a ferrous chloride solution. The ferrous oxalate was ignited in the air and reduced with hydrogen which had been purified by passage over pumice stone soaked in lead nitrate solution and over lumps of potassium hydroxide. McGillivray[72] also used the ferrous oxalate method of preparing a pure salt of iron, which was subsequently ignited and then reduced with hydrogen to form metallic iron. Although no analyses were given, McGillivray stated that the product invariably contained carbon and oxygen. He therefore considered the ferrous oxalate method inferior to the ferrous chloride method of purification. The ferrous oxalate method was studied in the early work at the Physikalisch-Technische Reichsanstalt,[136,152,170] but it was found that iron prepared from the oxalate invariably contained manganese, as did iron prepared from the formate. A subsequent report[186] stated that a sample of oxalate iron contained 0.025 per cent manganese, 0.03 per cent copper, and 0.06 per cent nickel.

Kreusler[180] used the oxalate method to prepare iron, for which he claimed high purity. Ferrous oxalate, precipitated from ferrous ammonium sulphate solution, was ignited and reduced with electrolytic hydrogen which was carefully purified, as were all the reagents used. The resultant iron contained sulphur if glass or porcelain tubes were used. These materials seemed to be attacked by the hydrogen with the formation of hydrogen sulphide which contaminated the metal. Therefore silica tubes were used and, as iron oxide attacks these, it was necessary to inclose the iron oxide in a boat made from pure iron foil. The final product was obtained by reducing in hydrogen, oxidizing again in a stream of pure air, reducing again with

hydrogen, and repeating this twenty times. As sulphur was still present in the product, Kreusler concluded that it came through the quartz tube from the flame used in heating and that electric heating would avoid the sulphur contamination.

The spongy iron was pressed into rods by hydraulic pressure and melted by passing an arc between two rods in a vacuum. The beads of iron [largest 8 mm. (0.3 in.) in diameter] were stated to be very pure. Kreusler did not report a detailed analysis but estimated that the total of metallic impurities did not exceed 0.0001 per cent and that the amount of sulphur present was extremely low. The material could be cold rolled or drawn and was similar to platinum in appearance. The beads were not noticeably attacked by hydrochloric acid but dissolved readily in nitric acid. No measurable amount of gas was given off during heating in a vacuum, nor were the electric and magnetic properties affected by such treatment. However, neither the temperature coefficient of electric resistance[180] nor the magnetic properties[177] indicate exceptional purity.

Crystallization of ferrous chloride also was employed to prepare a purified salt of iron that could be converted to the oxide, which in turn could be reduced to the metal. McGillivray's method,[72] which he preferred to the oxalate method, was to dissolve about 100 g. of iron wire, practically free from manganese, in pure hydrochloric acid, having a slight excess of iron. The solution was then diluted slightly and filtered into strong hydrochloric acid with agitation. The precipitated crystals of ferrous chloride were collected on asbestos wool, washed with a concentrated hydrochloric acid and sucked as dry as possible, after which the drying was completed between sheets of filter paper. The crystals were dehydrated by heating in a current of hydrochloric acid gas and finally were fused. After cooling, the melt was ground and the powder reduced with carefully purified hydrogen at a red heat.

The direct reduction of iron chlorides by hydrogen (Peligot's method[3]) was investigated by Bagdasarian.[699] The reduction by hydrogen of ferric chloride to ferrous chloride was detectable at 100°C. (210°F.) and was rapid at 200°C. (390°F.). The following are some of his results for the reaction between hydrogen or hydrochloric acid and fused ferrous chloride:

Reaction	Temperature		Equilibrium constant $K = \dfrac{p^2 HCl}{pH_2}$	Equilibrium concentrations in the gas phase	
	°C.	°F.		HCl, per cent	H₂, per cent
Ferrous chloride and hydrogen	702	1296	0.064	22.0	78.0
	800	1472	0.297	41.6	58.4
	925	1697	0.767	57.3	42.7
	932	1710	0.813	58.4	41.6
Iron and hydrochloric acid	725	1337	0.11	28.2	71.8
	1005	1841	1.87	72.1	27.9

Recent reports[1044, 1050A] from the National Physical Laboratory in England indicate that purification of ferrous chloride is the method there adopted for the preparation of a pure salt of iron. It was the former practice to electrolyze a solution of purified ferrous chloride with anodes of ingot iron and to subject the electrodeposited material to repeated melting in a vacuum and in hydrogen to eliminate gaseous constituents. The product, however, was contaminated by constituents of the ingot iron anodes; a sample which contained 0.022 per cent nickel, 0.02 per cent oxygen, 0.006 per cent carbon, 0.003 per cent chromium, 0.001 per cent phosphorus, 0.0008 per cent copper, 0.0005 per cent silicon, and no sulphur and manganese was considered to be of exceptional purity. To eliminate nickel the purified ferrous chloride is now decomposed with steam, with subsequent reduction of the oxide by means of hydrogen. The reduced iron is sintered, briquetted, and melted under hydrogen and finally melted in a vacuum. It is reported that, exclusive of oxygen, the total of impurities is 0.012 per cent, the chief impurities being 0.0045 per cent carbon, 0.003 per cent manganese, and 0.0006 per cent nickel. Determination of the properties of this iron is reported to be in progress.

After extended experimentation at the Physikalisch-Technische Reichsanstalt[136, 152, 170, 186, 202] with various methods of purification, it was decided that ignition of ferric nitrate, which had been purified by recrystallization, and reduction by hydrogen of the oxide formed offered the best means of obtaining pure iron.

In 1908, at the request of the Reichsanstalt, the firm of Kahlbaum prepared considerable quantities of iron by a modification of the above process. Carefully purified ferric nitrate crystals were melted at 50°C. (120°F.) and treated with gaseous ammonia with the formation of a dense red iron oxide and ammonium nitrate. After thorough washing to remove the ammonium nitrate, the oxide was ignited and reduced with hydrogen. The iron powder was melted in the oxyhydrogen flame. A rod of iron so made had the following composition: traces of carbon and silicon, 0.001 per cent of manganese, 0.004 per cent each of copper and nickel plus cobalt, and a few hundredths of 1 per cent of oxygen (as oxide). The ferric oxide produced by this method was undoubtedly of very high purity, as were some specimens of iron produced from the oxide. Great difficulty was experienced, however, in melting the reduced iron powder without introducing an amount of impurities which would destroy the value of the product. This difficulty apparently led the Physikalisch-Technische Reichsanstalt to abandon the production of iron by thermochemical means and to use electrolytic iron, furnished by the firm of W. C. Heraeus, in subsequent work on the properties of high-purity iron.

For use in studying the corrosion of iron, Lambert and Thomson[216] prepared iron of unusual purity by first depositing iron on iridium electrodes, from a solution of pure ferric chloride. After washing, the deposited iron was dissolved in dilute nitric acid and the ferric nitrate was crystallized by evaporation, filtered, and washed with concentrated nitric acid. The ferric nitrate was recrystallized four or five times, dried, and ignited in an iridium boat, which was then placed in a silica tube. The iron oxide was reduced with pure hydrogen at a temperature just above 1000°C. (1830°F.).

The hydrogen, prepared by electrolysis of a barium hydroxide solution, was passed over soda-lime and caustic soda. The Jena glass beakers and Gooch crucibles were cleaned by immersion for several weeks in concentrated nitric acid, and were kept in boiling nitric acid for several hours prior to using. The iridium boat was boiled with aqua regia and with concentrated nitric acid and was then ignited. The nitric acid was prepared by vacuum distillation, the distillate being discarded as long as non-volatile matter could be detected in a 50 cu. cm. sample.

Although Lambert and Thomson did not report analyses of their iron, it is generally considered to have been material of unusual purity, as a result of the careful purification of the iron salt and the extreme precautions which were taken to avoid introduction of impurities after the pure salt was once obtained. The iron did not rust in pure water and oxygen, even after several months' exposure, whereas iron that was prepared in similar fashion, except that the final reduction was carried out in platinum instead of in iridium, rusted readily as did iron prepared from commercial ferric nitrate. This unusual resistance to corrosion was cited as proof of the unusual purity of Lambert and Thomson's best samples; in fact this material played an important part in the controversy whether theoretically pure iron would or would not rust in pure water. This discussion is reviewed in more detail in the subsequent chapter on corrosion of iron.

A major difficulty encountered in the preparation of high-purity iron by reduction of iron salts with hydrogen is that the product, sponge iron, is susceptible to oxidation on contact with air, this susceptibility to oxidation increasing as the temperature of reduction is decreased. The presence of oxygen in reduced iron was discussed by Mylius[383] and by Schenck and Dingmann.[739] If the reduction is completed at temperatures below 710°C. (1310°F.), according to Smits and Wallagh,[634] or below 530°C. (985°F.), according to Tammann and Nitikin,[583] the resulting iron is pyrophoric, *i.e.*, the iron sponge is rapidly and completely oxidized on exposure to the atmosphere. If the reduction is completed at higher temperatures, the product is less susceptible to oxidation. Ruer and Kuschmann[803] found that 100 g. of iron reduced at 750°C. (1380°F.) absorbed as much as 30 mg. of oxygen when exposed to the air, but absorbed only 10 mg. if the temperature of the reduction was carried to 1000°C. (1830°F.). The tendency of the reduced iron to re-oxidize can be largely overcome by raising the temperature during the final stage of reduction to the sintering point, or preferably to the melting point, of the iron.

36. Preparation of High-purity Iron in Atomic Weight Determinations.—One of the procedures in determinations of the atomic weight of iron has been the production of a pure compound of iron and reduction of this compound to the metal. Determina-

tion of the atomic weight is based on the relation between the weights of iron and of the salt from which the iron was reduced. Several of the early determinations were based on the weights of metallic iron and iron oxide, but prior to the work of Richards and Baxter[97] the results of these determinations of atomic weight indicate either that the method was at fault or that the material was impure.

Richards and Baxter[97] were unable to develop a satisfactory method for preparing pure iron halides for the atomic weight determination. Instead they prepared pure iron oxide and determined the ratio between its weight and that of the metal obtained by reduction with hydrogen.

A solution of ferrous chloride was treated with hydrogen sulphide, and the precipitated heavy metals were separated by filtration. The solution was oxidized with nitric acid, and hydrated iron oxide was precipitated with ammonia and was washed. The precipitate was dissolved in sulphuric acid, and the solution was neutralized to precipitate basic ferric sulphate. This was dissolved in sulphuric acid, and the solution reduced electrolytically to form ferrous sulphate, which crystallized out. A solution of this ferrous sulphate was electrolyzed to deposit metallic iron, which was converted to ferric nitrate. After three recrystallizations, the ferric nitrate was converted to the oxide by heating at 150°C. (300°F.), crushing the cake formed, and finally igniting at 900°C. (1650°F.). A half-gram sample of the oxide was tested for the presence of nitrogen or oxides of nitrogen, yielding only a trace of gas. The oxide was then reduced with hydrogen.

The value 55.883 for the atomic weight of iron, which Richards and Baxter obtained from this material, was slightly higher than the value 55.84 which is now accepted. However, the difference is less than 1 part in 1000, and the results in general constitute an endorsement of the high purity of Richards and Baxter's iron as well as the excellence of their technique.

Recrystallization of ferric nitrate was the method used by Baxter and Hoover[253] for the preparation of pure iron oxide in a subsequent determination of the atomic weight of iron. All reagents used were carefully purified. Basic open-hearth iron was dissolved in nitric acid, and the solution was filtered through asbestos and evaporated to crystallization. The crystals were

separated from mother liquor in a platinum centrifuge. The nitrate was recrystallized four times from concentrated nitric acid. The crystals were then heated, forming a mixture of basic ferric nitrate and oxide, which was reduced with hydrogen. The reduction was carried out at a low temperature until no more water was evolved, the temperature was then raised gradually to 1100°C. (2010°F.) and was maintained at this point for several hours. About 60 hours' heating in hydrogen was necessary to obtain complete reduction; the loss in weight during 50 hours' further heating in hydrogen was negligible. The gain in weight of about 15 g. of the reduced iron upon standing in a desiccator ranged from 0.01 to 0.12 mg., indicating that little oxidation of the iron occurred upon exposure to air.

Baxter and Hoover's determination of 55.847 for the atomic weight of iron is accepted as one of the best which has been made, and is in excellent agreement with other good determinations which were based on the use of chlorides, bromides, or other salts of iron. Baxter and Hoover's iron is considered to be one of the purest irons ever produced, but this belief is based on factors other than direct analysis, as was the case with Lambert and Thomson's iron.

37. Hydrogen-treated Iron.—Iron of fairly high purity has been further purified with respect to certain constituents by treatment at elevated temperatures with hydrogen. Campbell, Ross, and Fink[502] found that treatment of iron with dry hydrogen at 950°C. (1740°F.) for 7 days lowered the carbon content from 0.018 to 0.009 per cent, and that treatment with moist hydrogen under the same conditions completely decarburized the iron. The phosphorus content was not affected by either treatment. Pfeil[801] completely decarburized iron containing 0.11 per cent carbon by 6 weeks' treatment with hydrogen at 750°C. (1380°F.). For the complete removal of oxygen from iron, Rooney[579] found that a temperature of 1150°C. (2100°F.) or more must be used for the hydrogen treatment; at temperatures between 900 and 1100°C. (1650 and 2010°F.), part of the oxygen was removed in 2 hr., but increase in the time of treatment did not result in further removal of oxygen. These findings of Rooney are not in agreement with the results of Baxter and Hoover,[253] who obtained complete reduction of iron oxide with hydrogen at 1100°C. (2010°F.), although 60 hr. were required.

Prolonged treatment of iron with moist hydrogen at temperatures between 1300°C. (2370°F.) and the melting point resulted in remarkably high magnetic permeability, according to Cioffi.[876,964]   He suggested that part of the improvement in magnetic characteristics was due to absorbed hydrogen but Yensen, in the discussion of Cioffi's papers, objected to this hypothesis and offered the counter-suggestion that the effect was entirely the result of purification of the iron.   Recent experiments, including those of Cioffi,[1049] confirm Yensen's contention and show that the improvement in magnetic characteristics is due primarily to the elimination or reduction in the contents of nitrogen and sulphur and, to a lesser extent, of carbon, oxygen, and phosphorus.   Practically all of the hydrogen absorbed at high temperatures is eliminated from the iron as it is slowly cooled; the residual hydrogen is without harmful effects on magnetic characteristics.   This subject is discussed in more detail in the chapter on magnetic properties.   Bain[957] reported that a sample of Cioffi's iron, which was prepared from open-hearth ingot iron by prolonged treatment with hydrogen at high temperatures, contained 0.028 per cent manganese, 0.005 per cent carbon, 0.004 per cent phosphorus, 0.003 per cent sulphur, 0.003 per cent oxygen, 0.0012 per cent silicon, and 0.0001 per cent nitrogen.   Comparison of these results with the usual analysis of open-hearth ingot iron indicates that, as might be expected, the treatment with hydrogen at high temperatures reduced the content of non-metallic elements such as carbon, sulphur, oxygen, and nitrogen but did not affect the contents of manganese and silicon.   Apparently the oxygen, sulphur, and nitrogen are removed more readily than is the carbon.   In some recent experiments* a sample of ingot iron was treated in undried hydrogen at 1365°C. (2490°F.), with the result that the oxygen, sulphur, and nitrogen contents dropped to 0.002, 0.003, and 0.0006 per cent, respectively, after 50 hours' treatment, but the carbon content was 0.006 per cent after 100 hours' treatment. The absence of siliceous materials and other refractories from the reaction chamber is advisable as these materials are reduced by hydrogen at the high temperatures employed, with consequent contamination of the iron.   Studies of the effect of prolonged

* Data submitted by Dr. R. F. Mehl, Carnegie Institute of Technology, in a private communication.

treatment with hydrogen at high temperatures on the composition and properties of carbonyl iron are reported to be in progress in several laboratories at the present time, but reports of these investigations are not yet available.

38. Reduction with Carbon and Carbon Monoxide.—Swedish charcoal iron is a product of the refining, by oxidation and slagging of impurities, of impure forms of iron obtained by carbon reduction. The method of manufacturing Swedish charcoal iron is described in many of the iron and steel handbooks; Danielson,[550] in an article published in 1924, gave an excellent description of the manufacture and properties of this iron. The impurities, he stated, lie between the following limits:

Element	Percentage
Carbon	0.02 to 0.06
Manganese	Trace to 0.10
Silicon	0.02 to 0.04
Phosphorus	0.04 to 0.07
Sulphur	0.005 to 0.010

Varying quantities of slag also are present. In the discussion of Dyer's paper,[53] analyses of Swedish charcoal irons were given in which the iron content, by direct determination, ranged from 99.900 to 99.945. Such analyses represent commercially pure metals rather than the extreme purity obtained in laboratory samples.

Charcoal iron which was imported from Sweden formerly was preferred for uses such as the manufacture of boiler tubes because it was tough and tubes made from it were less likely to split in expanding and beading during use in a boiler. However, domestic charcoal iron has gradually supplanted the imported product; in the last twenty years very little Swedish iron has been used for this purpose.*

39. Open-hearth Ingot Iron.—Open-hearth ingot iron, like Swedish charcoal iron, is a result of the oxidation and slagging of impurities in iron produced by carbon reduction. The first successful production of ingot iron in the basic open-hearth furnace seems to have been by Dyer[53] in 1892. With a charge

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* Private communication from Mr. G. H. Woodroffe, Metallurgical Engineer, Reading Iron Company, Reading, Pa.

of 50 to 80 per cent of scrap iron and 50 to 20 per cent of Swedish pig iron, he produced an iron of the following composition:

Element	Percentage
Carbon	Trace
Silicon	0.005
Manganese	Trace
Phosphorus	Trace
Sulphur	0.015

Lime was added to the slag at frequent intervals to ensure its basicity. Great care and watchfulness were necessary, as the metal was liable to eat through the furnace, several melts being lost in this way. In Dyer's opinion, this tendency made the production of ingot iron too risky and difficult to be of commercial value.

A process for the production of ingot iron in the basic open-hearth was developed successfully by Carnahan. This process, which was described by Carnahan (U. S. Patents 940,784 and 940,785, November 23, 1909), Cushman,[234] Aupperle,[205] Beck,[430] and Boylston,[766] differs from the methods used in the production of mild steel in the maintenance in the furnace of strongly oxidizing conditions, with additions of iron ore to oxidize the impurities in the melt, and the use of a strongly basic slag to remove the oxidized impurities. Deoxidation is effected by additions of pig iron just previous to tapping the furnace and by addition of aluminum in the ladle. The properties of this type of product were described by Kenyon.[787]

Open-hearth ingot iron is more widely used and is produced in much larger quantities than are other forms of iron which are roughly comparable in purity, for example sponge iron or charcoal iron. In view of the complex nature of iron ores, and the difficulty encountered in purifying iron, open-hearth ingot iron is a commercial product of surprisingly high purity. The analysis of basic open-hearth ingot iron, represented by the standard sample of ingot iron No. 55 of the National Bureau of Standards, is as shown in the table at the top of page 72. The presence of so many elements in detectable amounts is evidence of unusual care and completeness in the analysis rather than of impurity of this particular specimen. A number of the elements which were found to be present in this specimen ordinarily are not determined in the analysis of ferrous materials.

Element	Percentage
Carbon	0.013
Manganese	0.019
Phosphorus	0.003
Sulphur	0.017
Silicon	0.001
Copper	0.041
Nickel	0.020
Chromium	0.002
Molybdenum	0.002
Cobalt	0.006
Arsenic	0.012
Aluminum	0.002
Tin	0.008
Antimony	0.002
Oxygen	0.07
Nitrogen	0.0045
Total of determined impurities	0.2225

40. Sponge Iron.— Sponge iron, the product of the low-temperature reduction of iron ore, is not a particularly pure material; an iron content of 98 per cent is about the maximum obtained.   Owing to the method of manufacture, however, the impurities, with the exception of sulphur, are largely unreduced and are present as particles of gangue mixed with the iron but not combined or alloyed with it as in the product of a smelting operation.   When sponge iron is melted many of the impurities rise to the surface and form a slag, leaving a comparatively pure metal.   For example, in some experiments (unpublished) at the National Bureau of Standards a sample of Swedish sponge iron, after simple melting in an electric furnace, contained the following fixed impurities:

Element	Percentage
Carbon	0.030
Manganese	0.005
Phosphorus	0.002
Sulphur	0.037
Silicon	0.005

The great number of processes which have been devised for the production of sponge iron may be divided into two classes: those in which the reducing agent is employed in the form of coke or coal, and those using gaseous reducing agents such as

carbon monoxide, hydrogen, or mixtures of the two gases. The different processes have been reviewed by Wickenden,[459] Whitfield,[538] Fornander,[555] Flodin,[606] Edwin,[658] Hodson and Smalley,[720] Longmuir,[728] Wiberg,[752] Williams, Barrett, and Larsen,[753] Wüst,[755] Waterhouse,[869] Bull-Simonsen,[963] and Kunze,[974] but, of all the proposed processes, only those of Sieurin, of Thornhill-Anderson, and of Edwin seem to have achieved any degree of successful and continued commercial operation. The ensuing discussion is limited mainly to applications of these three processes.

The Höganäs Billesholm, A.B., at Halsingberg, Sweden, began large-scale production of sponge iron about 1911, according to Handy,[283] using a process developed by their chief engineer, Sieurin. A Hoffman ring furnace, of the type used in the ceramic industry, was fired with gas from a low-grade Swedish coal. Saggers charged with alternate layers of iron ore and coal were run on cars into the charging compartment of the kiln, whence they passed in order through the preheating, reducing, cooling, and discharging compartments. The gases passed in the direction opposite to that of the charge, the air for combustion entering at the discharge end, where, in cooling the reduced charge, it was preheated. The gases from the reducing compartment passed through the preheating chamber and left the kiln at a temperature of 150 to 200°C. (300 to 390°F.). After reduction the sponge iron was concentrated magnetically and pressed into "pigs."

The ore used was slime from the Gillivare iron ore and contained about 70 per cent of iron with 0.010 per cent of phosphorus and 0.002 per cent of sulphur. A low-grade coal, with about 35 per cent of ash and from 0.5 to 1.0 per cent of sulphur, was used for the reduction. To reduce sulphur contamination of the sponge iron, lime was mixed with the coal used in the charge. About 1.7 tons of coal were used for heating and reducing, per ton of sponge iron produced.

The production by the Höganäs Billesholm, A.B., in 1925 was about 15,000 tons per year. Fornander[555] stated that a plant using the Sieurin process was in operation in Japan, with a production of 20,000 tons per year.

To utilize the iron sands at Kuji, Japan, which owing to their fineness (95 per cent through a 65-mesh screen) are not a suitable

material for the blast furnace, a sponge-iron plant using the Thornhill-Anderson process[698,759] was constructed, with a capacity of 100 tons per day. The furnace had a slowly rotating circular hearth 3.65 m. (12 ft.) in diameter, heated indirectly by producer gas that was burned in 72 carborundum tubes. Iron sand and partially coked coal were charged continuously onto the hearth. During the 30 min. required for the passage of the charge across the hearth, the iron was reduced and thereafter was discharged from the hearth into a rotating tube externally cooled with water. After magnetic concentration, the sponge iron was briquetted under a pressure of 2800 to 3500 kg. per sq. cm. (40,000 to 50,000 lb. per sq. in.). The density of the briquettes was about three-fourths that of iron. The briquettes could be charged directly to the steel furnace as they sink below the slag line.

As recently as 1927, the A/S. Norsk Staal at Trondhjem, Norway, were using the Edwin process[658,697] for the manufacture of sponge iron. The unique feature of this process consisted not in the method of reduction but in the method of regenerating the gas. The spent gas was passed with a strong whirling motion through a tube several meters long in which a high-tension arc was maintained. The carbon dioxide reacted with carbon, injected in the form of crude oil, hydrocarbon gases, tar or even powdered coal, to form carbon monoxide. For the reaction to be efficient, the gases must leave the regenerator at a temperature of 1600 to 1700°C. (2910 to 3090°F.) which is too high for use in the kiln. This excess heat was utilized by passing the gases through a layer of coke or coal, completing the reduction of carbon dioxide to carbon monoxide, and reducing the temperature of the gas, which then passed through the reducing furnace, a rotary kiln. The preheated ore passing through the kiln was reduced with the production of carbon dioxide. The spent gas passed from the kiln to a recuperator where it was cooled to about 200°C. (390°F.) in heating the gas going to the regenerator. The cooled gas then entered the storage bell.

An excess of carbon monoxide was generated continually in this process, and considerable water vapor also was formed. To eliminate the excess of carbon monoxide, from 10 to 15 per cent of the spent gas was passed over a catalyst, which caused the carbon monoxide and water to react, with the formation of

hydrogen and carbon dioxide. The latter was removed, and the hydrogen was returned to the system.

An installation of the Norsk-Staal process at Bochum, Germany, was described by Bull-Simonsen[963] and by Kunze.[974] Trays of ore were preheated in the first of three furnaces, reduced in the second furnace, and cooled in the third. The reducing gas consisted of 40 per cent hydrogen and 60 per cent carbon monoxide. The sponge iron was briquetted for use as melting stock for the production of electric-furnace steel. Production was reported[974] to be 38 tons of sponge iron per day, but, according to Bull-Simonsen,[963] the success of the operation was doubtful from an economic point of view. Private communications to the authors indicate that the Bochum plant is not now (1935) in operation.

Large-scale experimentation with the Hornsey-Wills process[542] was conducted at Lorain, Ohio, by the United States Steel Corporation.[648] The ore passed continuously through three kilns; in the first it was preheated, reduction took place in the second, and the product was cooled in the third. A countercurrent system was used, the reducing gases entering at the discharge end of the cooler. Sealed ends of the kilns prevented entrance of air and allowed reducing conditions to be maintained throughout the operation.

In 1928 the Ford Motor Company was reported[758] to have been licensed to manufacture sponge iron by a method developed by W. H. Smith, the patent rights for the process being held by The General Reduction Company. As described by Waterhouse,[869] the ore was crushed smaller than $\frac{1}{4}$ in. and was mixed with a carbonaceous material and charged in a furnace similar to a coke oven. After preheating by the waste gases the charge passed to the reduction zone, where a temperature of 870 to 980°C. (1600 to 1800°F.) was maintained. In the cooling zone it met the incoming air for combustion and was discharged below 120°C. (250°F.).

A study of the production and use of sponge iron is now in progress in the laboratories of the United States Bureau of Mines.[1050] A recent publication[1077] on this investigation describes the improvement in composition which results from heating the sponge iron to welding temperature and squeezing out the slag.

On account of its physical structure, the principal use of sponge iron is as a melting base, particularly in the manufacture of electric-furnace steel. Of lesser importance is its use for "cementing out" copper and lead from solutions of salts of these metals, the large surface area of the sponge making it an efficient precipitant. A vacuum-melted sponge iron, stated to contain 99.93 per cent iron, has been marketed under the trade name "Svea Iron."[991] Its principal application reported to date is in the manufacture of vacuum tubes. When polished it is said to show high resistance to corrosion.

41. Reduction by Metals.—The precipitation of iron from solution by a metal higher in the electromotive series, such as zinc[1] or manganese,[59] would hardly be expected to yield a product of high purity in view of the probable contamination by insoluble impurities from the precipitating metal, by salts in the solution, and by oxygen in drying. Nor would exceptional purity be expected of iron prepared at elevated temperatures by reduction of iron salts with metals, for example the reduction of ferrous chloride with zinc vapor,[8] the reduction of iron oxide by aluminum as in the Goldschmidt process,[78] the reduction of the oxide by calcium as reported by Perkin and Pratt[163] or by sodium as proposed by Hiorth (Norwegian Patent 18,750, of 1908).

42. Summary of Reduction Methods.—In the preparation of high-purity iron by chemical methods, reduction with pure hydrogen is the most practical method of converting a purified compound of iron, usually the oxide, to the metallic state. Reduction can be completed at relatively low temperatures, but it is advisable to carry the temperature of reduction to 1000°C. (1830°F.), or preferably even higher, to decrease the susceptibility of the reduced iron to oxidation. Reduction with hydrogen does not affect the content of metallic impurities, consequently the purity of the reduced iron cannot exceed the purity of the oxide or other salt of iron. The irons prepared by Lambert and Thomson[216] and by Baxter and Hoover,[253] by reduction of the oxide obtained from an elaborately purified salt of iron, are considered to be two of the purest specimens of iron ever obtained. This belief is based upon the precautions observed in the preparation and upon some of the observed properties; analyses of the products were not made.

Processes for the reduction of iron ore, either in smelting operations or in the production of sponge iron, have been designed for the production of iron on a commercial scale, rather than for the production of metal of utmost purity.   The product of these processes in some cases is of satisfactorily high purity for a product of large-scale operations but has not been comparable in purity with the best irons produced by other methods.

Iron can be produced by the reduction of its compounds by means of various metals, but such processes are not successful either in the production of high-purity iron or in the economic production of iron in commercial quantities.

B. THERMAL DECOMPOSITION OF IRON CARBONYL

The volatility of iron carbonyl and the facility with which it is decomposed into iron and carbon monoxide make it a possible medium for the purification of iron.

The preparation of any considerable quantity of iron carbonyl by the first method of Mond,[49,50] who discovered the compound in 1891, was an extremely tedious process.   Pyrophoric iron, made by hydrogen reduction of the oxide, prepared from the oxalate, was treated with carbon monoxide at room temperature until no more gas was absorbed.   The temperature was then raised to 120°C. (250°F.), the iron carbonyl was distilled off, and the process was repeated.   Mond, Hertz, and Cowap,[218] in 1920, published results of a study of the effect of temperature and pressure on the reaction.   With pressures from 150 to 300 atmospheres the formation of iron carbonyl was greatly accelerated by increase in temperature up to 200°C. (390°F.), but above that temperature the yield decreased because of decomposition. Similar information was disclosed in Mond's patent of 1908 (British Patent 17,608, August 21, 1908), by Stoffel[249,316] in 1911 to 1914, and by Mond and Wallis[480] in 1922.

With added experience in high-temperature high-pressure technique for gas reactions, obtained in developing the Haber-Bosch process for the synthesis of ammonia, the Badische Anilin und Soda Fabrik about 1924 began manufacture of iron carbonyl on a large scale.   DeLangeron,[726] in a paper published in 1927, stated that the temperature used was 140°C. (285°F.) at 50 atmospheres pressure.   The iron prepared by hydrogen reduction of iron ore was treated with either pure carbon

monoxide or producer gas. The principal use for the iron carbonyl formed was as an "anti-knock" compound for use in motor fuel. DeLangeron's paper includes a summary of the properties of iron carbonyl and an excellent bibliography.

Beginning with 1924, a number of patents were granted to the I. G. Farbenindustrie, A. G., covering processes of preparing iron carbonyl and methods of preparing "pure" iron from it. Mittasch,[796] in 1928, published a description of the process used by the Farbenindustrie for the production of carbonyl iron. Carbon monoxide, under pressure, was circulated over reduced iron at a temperature of 150 to 200°C. (300 to 390°F.), the carbonyl was separated by condensation, and the carbon monoxide returned to the reaction chamber. The carbonyl was decomposed by injecting it into a hollow vessel heated to 250°C. (480°F.). The iron was produced in a finely divided form with particle diameters of less then 0.001 mm. (0.000039 in.). Another method of obtaining iron from iron carbonyl, patented by Farbenindustrie (British Patent 281,963, June 25, 1927), was to pass the liquid or gaseous carbonyl into paraffin, paraffin oil, pyridine, or salts heated to 270°C. (520°F.), or into molten lead or iron. Processes for recovering the finely divided iron which remained suspended in the gas stream after thermal decomposition included electric or magnetic precipitation, or passing the gas through paraffin oil (British Patent 269,677, January 23, 1926).

According to Pincass,[852] the Farbenindustrie in 1929 used a process in which the reduction of the iron ore and formation of the carbonyl were completed in one operation. Producer gas or water gas, with a hydrogen content of at least 5 per cent, was used to treat the ore under a pressure of 200 atmospheres at about 500°C. (930°F.). Careful regulation of temperature and pressure was necessary, and it was important that the gas velocity was such that not over 6 per cent by volume of iron carbonyl was present. According to Pincass, the carbonyl iron was used for the preparation of an iron catalyst for the synthesis of ammonia.

A recent description of the commercial production of carbonyl iron in Germany is found in an article by Winter.[1039]

Iron made by decomposition of the carbonyl contains up to 1 per cent of carbon. It is reported that, to purify the iron, it is mixed with pure iron oxide, prepared by catalytic oxidation of

iron carbonyl, in such proportions that when melted under vacuum in a high-frequency furnace both carbon and oxygen are eliminated. Mittasch[796] stated that no sulphur, phosphorus, copper, manganese, nickel, cobalt, chromium, molybdenum, zinc, or silicon could be detected in this material by the most accurate analytic methods and that some iron had been prepared with a carbon content as low as 0.0007 ± 0.00016 per cent and with an oxygen content of less than 0.01 per cent. The electric and magnetic properties were stated to be excellent.

The proponents of carbonyl iron claim that almost absolutely pure iron can be obtained by this process, but to date there is not enough information available to permit the unqualified acceptance of this claim. Two samples, of carbonyl iron, which were considered to be unusually free from metallic impurities were obtained recently through the courtesy of the Naval Research Laboratory, Washington, D.C., and the Metals Research Laboratory of the Carnegie Institute of Technology. Spectrochemical examination showed that nickel, copper, magnesium, aluminum, silicon, and calcium were present in one sample, and that copper, manganese, silicon, molybdenum, tin, chromium, nickel, magnesium, and aluminum were present in the other. Chemical analysis of the latter material confirmed the presence of seven of the nine metallic impurities and in addition showed that carbon, sulphur, phosphorus, oxygen, nitrogen, and hydrogen were present in small but detectable amounts, although the material had been subjected to a purification treatment in hydrogen at high temperatures. The major impurity in this sample was copper, which was present to the extent of 0.035 per cent; the other metallic impurities ranged from 0.008 per cent of manganese to 0.002 per cent each of nickel and of chromium. The copper content alone would disqualify this sample from classification as an extremely pure iron, although it is possible that the observed copper content was the result, at least in part, of contamination which occurred during the treatment in hydrogen at high temperature. Additional analyses should be made to determine the composition of representative samples of carbonyl iron.

The thermal decomposition of other compounds of iron is possible; for example, van Arkel[1075] described the production of iron by heating iron iodide in an evacuated glass apparatus

which contained a heated filament. The thermal decomposition of compounds of iron, other than iron carbonyl, has attracted little attention to date.

The production of purified iron by sublimation processes has received relatively little attention. A recent report by Kroll[1060] concludes that the production of very pure iron, by means of a sublimation process, is not feasible on account of the distillation of impurities as well as of iron.

C. MELTING OR COMPACTING

Iron of high purity that is obtained by electrolytic or thermo-chemical processes usually must be melted to become available in useful forms. Molten iron reacts with avidity with many materials, consequently great difficulty is encountered in maintaining the quality of high-purity iron during a melting operation. Contamination of the melt may result from the products of combustion in fuel-fired furnaces, from the vapors from the resistor in electric resistance furnaces, or from the refractory used to contain the melt. Contamination from the products of combustion or from resistor vapors can be avoided by the use of high-frequency induced currents,[597,598,767,931,932,933] or by other means,[180,619] but contamination from the refractory container remains an important possibility. The choice of refractories is limited to materials which will withstand temperatures in excess of 1500°C. (2730°F.) and which are free from impurities that will contaminate the melt.

The danger of contamination of the metal naturally is not so serious in compacting as in melting operations as the former are carried out at relatively low temperatures.

43. Melting.—Contamination of the metal by the products of combustion was encountered in early attempts to melt purified iron sponge in gas-fired furnaces.[186,349] Furnaces heated by various types of electric resistance units were tried[321,349] but yielded contaminated products. Heating the metal by means of induced high-frequency currents possesses obvious advantages for this type of melting operation and has been recommended by a number of workers.[597,598,673,767,931] The atomic hydrogen flame was used by Langmuir[619] to melt small rods of iron without danger of contamination by carbon, oxygen, or nitrogen, and

Kreusler[180] melted purified iron by passing an arc, in a vacuum, between two rods of compressed iron powder.

Magnesium oxide has been selected by a number of investigators as the best available refractory for the melting of high-purity iron. The workers at the Physikalisch-Technische Reichsanstalt[186] in 1908 were unable to prepare satisfactorily dense crucibles, but the technique of crucible preparation has been improved since that time. Directions for the preparation of small magnesia crucibles, bonded with a solution of magnesium chloride, were given by Jordan, Peterson, and Phelps[673] and by Swanger and Caldwell.[946] The use of alcoholic shellac as a binder for magnesia crucibles was described by Mehl, Whitten, and Smith,[624] but it appears that the presence of organic matter in the refractory would be at least a potential source of contamination by carbon. Crucibles may be formed either by tamping by hand or by molding under pressure. The crucibles are usually air dried, baked, and finally fired in gas or electric furnaces. Tritton[637] prepared unusually dense molds by maintaining an arc between two carbon electrodes in the center of the rapidly rotating mold. The resulting crucibles had a porcelain-like structure and were reported to be capable of holding molten iron oxide.

Electrically fused magnesia was used by Yensen[321] in 1913 for the production of crucibles in which electrolytic iron was melted in an Arsem vacuum furnace. This material, however, contained about 2 per cent of silica. Cain, Schramm, and Cleaves[349] subsequently found that the presence of as little as 0.05 per cent of silica in the magnesia resulted in noticeable contamination of the melt by silicon. Cain, Schramm, and Cleaves were forced to apply additional purification to the best magnesia obtainable at the time of their experiments, but subsequent investigators[673,946] found that the quality of commercial magnesia had been improved and that the chemically pure or reagent grade was satisfactorily free from impurities. Other grades of magnesia, such as the fused magnesia of commerce, were not sufficiently pure.

Pure lime, alone or mixed with other refractories, was tried[186] without great success as a refractory for melting high-purity iron. Alumina, zircon, and zirconia have been tried,[186,673,946] but in general, these materials have not been available in sufficient

purity. However, a recent report by Turner[1074] describes the use, with satisfactory results, of aluminum oxide which was exceptionally pure; a trace of iron was the only appreciable impurity. Electrically fused thoria is an excellent refractory,[946] suitable for melting purified iron, but is difficult as well as expensive to prepare. Beryllium oxide, a relatively new refractory, appears promising, as it is somewhat more refractory than magnesia and does not volatilize so readily, according to Swanger and Caldwell.[946]

The consensus of opinion appears to be that pure grades of magnesia have constituted the cheapest available satisfactory refractory for melting high-purity iron. The properties of thorium oxide are excellent, in some respects superior to magnesia, but thoria is not so readily available and is decidedly more expensive than magnesia. The limited information available to date, regarding refractory uses of beryllium oxide, indicates that this material may be useful as a refractory in the melting of very pure metals.

44. Compacting.—Sauerwald[580] obtained solid iron by applying pressures up to 5000 atmospheres to thin layers of iron powder. He ascribed the cohesion of the particles after release of the pressure to atomic affinity between particles brought into close proximity. Upon heating the iron so obtained, the tenacity increased with increase in temperature up to a maximum, after which it decreased with further increase in temperature. There was a notable increase in grain size when the metal was heated to temperatures near its melting point.

A method of obtaining solid iron by compressing "pure" iron powder, such as carbonyl iron, under high pressure, treating it in a reducing atmosphere at a suitable temperature, and working it mechanically was described by Schlecht, Schubardt, and Duftschmidt.[940,965]

Processes for obtaining solid iron from sponge or powdered iron, without melting, have not been developed beyond the experimental stage.

D. PREPARATION OF SINGLE CRYSTALS

Large single crystals of a metal are valuable for the determination of the constants of the material itself rather than an average of the properties of a number of crystals oriented in all directions,

each deformed by, and its properties affected by, the others. Large single crystals of iron occasionally have been found[654] in ingots or "skulls," but the crystal formation usually was imperfect and the occurrence of these large crystals was accidental.

Methods for the laboratory preparation of large single crystals of metals have been described by Carpenter[654] and by Van Liempt.[808] Carpenter classified the general methods into three groups, according to the formation of the crystals from the gaseous, liquid, or solid state. Van Liempt added a fourth method of growing large single crystals, by electrodeposition on a small single crystal. Most of the large crystals of iron that have been made in the laboratory have been prepared from the solid state by recrystallization of strained polycrystalline material in the so-called "strain-anneal" method. Deposition from the gas phase is difficult to control; deposition of single crystals from the liquid state is considered to be feasible only for metals which do not have allotropic modifications in the solid state; and, according to available information, electrolytic deposition on a small single crystal of the metal has not been used for the preparation of single crystals of iron.

45. Formation from the Gas Phase.—Fischvoigt and Koref[605] prepared single crystals of metals by deposition on a heated filament from a mixture of the gaseous metal chloride and a large excess of hydrogen. The apparatus and details of the method, particularly as applied to the growth of single crystals of tungsten, were described by Koref.[477] No details of the preparation of single crystals of iron were given, other than the statement that if the filament was heated to 900 to 1400°C. (1650 to 2550°F.) only unoriented polycrystals of gamma iron were deposited, but with the filament below 900°C. (1650°F.) single crystals of alpha iron could be grown.

46. Formation from the Solid Phase.—Edwards and Pfeil[553] developed a method of preparing single crystals of iron, based on the work of Carpenter and Elam on aluminum. This, in turn, was based on the observation of previous workers, notably of Sauveur,[265] that there was an abnormal grain growth in metals when they were strained beyond the elastic limit and subsequently annealed. The procedure found by Edwards and Pfeil to give the maximum crystal growth in iron was as follows: The iron was heated at 950°C. (1740°F.) for 48 hr. in an atmos-

phere of moist hydrogen, and was then slowly cooled (for 12 hr.) to 100°C. (210°F.). This treatment produced decarburized material with a grain size of about 120 grains per sq. mm. In a later paper, Edwards and Pfeil[603] modified the normalizing procedure and obtained the same grain size by decarburizing at 875°C. (1605°F.) for 48 hr. and heating to 1000°C. (1830°F.) for 12 hr., followed by slow cooling. The iron was then strained in tension to an elongation of 3.25 per cent, after which it was annealed at 880°C. (1615°F.) for 72 hr.

Single crystals of iron so prepared were invariably coated with a polycrystalline layer. If this surface coating was removed by careful filing to reveal the structure, the specimen could be heated to 880°C. (1615°F.) without recrystallization as a result of the cold work. If the decarburized iron plates were first deformed by cold rolling, annealing produced single crystals without the surface coating of polycrystals. The latter behavior indicated that the surface crystals of the metal possessed some capacity of altering their shape without acquiring the peculiar kind of strain or change which makes abnormal growth possible during annealing.

The iron used by Edwards and Pfeil for preparing single crystals was not particularly pure, as it contained 0.13 per cent of carbon, 0.23 per cent of silicon, and 0.44 per cent of manganese. The carbon content of the material after decarburization was not determined, but it was reported that the presence of carbon could not be detected by microscopic examination. In another paper, Pfeil[681] reported that a single crystal 5.5 in. in length by 0.5 in. in diameter and numerous crystals between 1.5 and 3 in. in length by 0.5 in. in diameter were obtained from a mild-steel bar which contained 0.10 per cent of carbon, 0.064 per cent of silicon, 0.46 per cent of manganese, 0.034 per cent of sulphur, and 0.02 per cent of phosphorus.

Osmond and Frémont[134] in 1905 isolated single crystals of iron as large as 1.5 in. long by 0.75 in. in diameter from a rod used as a buckstave in an open-hearth furnace, and determined their properties. They found that the iron had been completely decarburized and the impurities largely slagged out, leaving almost pure iron. In discussion of Edwards and Pfeil's paper[553] O'Neill suggested that the combined effect of the straining of the iron by the heating and cooling of the furnace and the annealing

due to the heat of the furnace was the cause of the crystal growth observed by Osmond and Frémont.

The method of Edwards and Pfeil was applied to vacuum-melted electrolytic iron by Gries and Esser.[831]   They found that the optimum conditions were about the same as those specified by Edwards and Pfeil, namely, a grain size of 120 to 140 grains per sq. mm., the use of tension rather than compression as a method of deformation, and an elongation of 3.00 to 3.25 per cent.   The maximum crystal growth was completed in 48 hours' annealing at 880°C. (1615°F.).   Edwards and Pfeil found that the presence of carbon was detrimental to crystal growth and Gries and Esser found the presence of oxygen equally detrimental.

Ziegler[913] used electrolytic iron that had been melted under vacuum and deoxidized by addition of carbon in an attempt to prepare, by the method of Edwards and Pfeil, round tensile test pieces composed of large iron crystals.   The attempt was unsuccessful as there was obtained merely a shell composed of large crystals surrounding a core of polycrystalline material. It was concluded that the strain was not uniform across the cross-section of a round tensile test piece.   Ziegler's failure to obtain large single crystals comparable to those obtained by Pfeil may have been due, at least in part, to the fact that Ziegler used electrolytic iron which was of higher purity than the mild steel used by Pfeil.

In another experiment, a series of flat test pieces, prepared from basic open-hearth ingot iron, was normalized in moist hydrogen at 950°C. (1740°F.), strained to 2 to 4 per cent elongation, and then annealed at 850°C. (1560°F.) for 72 hr.   The greatest grain growth was obtained after elongation of 2.25 to 2.50 per cent, which is somewhat less than the 3.25 per cent recommended by Edwards and Pfeil.   Ziegler thought that this difference might have been caused by a small variation in the properties of the original material as well as in the process of preparation.

For use in magnetic tests, Ziegler made a series of rings, $\frac{1}{2}$ in. (13 mm.) high, $\frac{5}{8}$ in. (16 mm.) in outside diameter, $\frac{3}{8}$ in. (9.5 mm.) in inside diameter, of vacuum-melted electrolytic iron.   These rings were normalized in moist hydrogen at 950°C. (1740°F.) for 24 hr., subjected to pressures of from 21,000 to

23,000 lb. per sq. in. (1480 to 1620 kg. per sq. cm.) and re-annealed at 850°C. (1560°F.) for 72 hr. No single-crystal rings were obtained and only two rings became macrogranular. Exactly the same treatment which gave macrograined rings in some cases gave rings composed of microcrystals in others, indicating that there were unknown factors present which retarded abnormal crystal growth.

A method for the growth of large crystals in solid polycrystalline iron, but differing from the usual strain-anneal method, was devised by McKeehan.[732] His method was based on control of the rate of recrystallization during the transformation of gamma to alpha iron. A portion of the length of an iron wire was heated to 1400°C. (2550°F.) or more by means of an electric current which entered and passed from the wire through sliding contacts. When the wire reached the desired temperature it was moved along, through the sliding contacts, with the result that one end of the heated portion passed beyond the contact and cooled off while an equivalent length of cold wire entered the heating zone through the other sliding contact. The rate of cooling of the wire and consequently the rate of passage through the gamma-alpha transformation was controlled by the rate of travel of the wire through the contacts. At a favorable rate of travel single crystals 20 cm. (7.87 in.) or more in length could be obtained in an iron wire 1 mm. (0.039 in.) in diameter. Crystals were prepared in vacuum and in hydrogen, the best results being obtained in hydrogen at atmospheric pressure. Electrolytic iron was used in most of the work, although some crystals were grown in iron which originally contained 0.8 per cent of carbon. The purity of the iron and its previous mechanical history were of little importance but any torsion or irregularity in the tension resulted in twinning. Polycrystalline surfaces, which were usually encountered in the strain-anneal method, were not present in the wire.

47. Summary of the Preparation of Single Crystals.—Determination of the properties of single-crystal specimens obviously is the best way to determine the basic properties of the metal. In ordinary polycrystalline metal a determination of a property is merely the average of the properties of a large number of crystals variously oriented. In many cases the properties of a metal vary with the crystal orientation.

The development of large single crystals of iron by slow cooling from the liquid state is not considered practicable, owing to the transformations and the consequent recrystallizations which occur in solid iron. The strain-anneal method has been successfully employed to develop large crystals of iron by recrystallization in the solid state. Best results have been obtained with thin strip specimens, strained in tension. Satisfactory results have not been obtained with thicker specimens of high-purity iron nor with specimens strained in compression.

Long single crystals of iron, in a wire 1 mm. (0.039 in.) in diameter, have been developed by controlling the rate of passage through the gamma-alpha transformation, but there is no record of attempts to apply this method to specimens other than wires of small diameter.

Single crystals of iron are not necessarily pure iron. Any element which is soluble in solid iron may be present in a single crystal in amounts up to the limit of solid solubility of that element. Electrolytic iron is the purest form of iron which has been used for the preparation of single crystals.

E. AUTHORS' SUMMARY

Probably the purest specimens of iron that have ever been prepared were those of Lambert and Thomson[216] and of Baxter and Hoover.[253] Each of these irons was prepared by reduction with purified hydrogen of iron oxide obtained from ferric nitrate that had been subjected to an elaborate process of chemical purification. In each case only small amounts of the metal were prepared and the estimation of the purity of the product is based mainly on the care and precautions observed in the preparation; chemical analysis was not feasible on such small samples.

Recrystallization of ferric nitrate has been employed with better success for the preparation of a pure salt of iron than has crystallization of other salts such as ferrous oxalate, sulphate, chloride, and formate. The product of these laboratory purification processes is spongy or powdered iron, obtained by reduction of the purified salt or oxide with hydrogen. The chemical activity of this product, even at low temperatures, necessitates protection from oxygen and other elements with which it might react. The conversion of spongy or powdered iron to solid

metal without loss in purity is difficult and requires careful selection of materials and procedure.

Certain non-metallic constituents can be largely or completely eliminated from solid iron by extended exposure to hydrogen at high temperatures, but metallic impurities, if present, generally are not affected by this treatment.

The purity obtained in commercial products such as charcoal iron, sponge iron, and open-hearth ingot iron is comparable in some respects with that of commercial electrolytic iron but is not comparable with the purity obtained in laboratory products. Claims of extraordinary purity have been made for iron produced from iron carbonyl, but authentic information to substantiate these claims is not yet available.

Single crystals of iron can be prepared for use in determining the basic properties of the metal. The preparation of single crystals, however, is not a purification process and the single crystals so far prepared have been made from iron of only commercial purity.

The preparation of iron of extreme purity, approaching absolute purity as nearly as possible, and in quantities large enough to be useful, is an end still to be sought.

PART II
THE PROPERTIES OF HIGH-PURITY IRON

INTRODUCTION

In this age of Iron and Steel, iron in one form or another is a familiar essential of our everyday life. It has been estimated recently[1029] that the amount of steel now in use throughout the world is about 1200 million tons, of which 700 million tons is in use in the United States. In view of the wide use of ferrous materials, it would seem that the fundamental properties of iron, on which the properties of all commercial irons and steels are based, would have been accurately determined long ago, but such is not the case. Some of the atomic properties of iron can be defined with certainty: it is element number 26 in the periodic table and is placed in the eighth group, associated with cobalt and nickel; its atomic weight is 55.84;[1047] it forms two series of chemical compounds, the ferrous series in which the iron is bivalent and the ferric series in which it is trivalent; there are two isotopes of iron,[992] a principal isotope of mass 56 and a rarer isotope of mass 54, the latter being about 5 per cent as abundant as the principal isotope; the chemical reactions of iron have been carefully studied. However, even a casual survey of existing literature shows that the fundamental technologic properties of iron—mechanical, thermal, electric, and magnetic— cannot be stated with the precision which might be expected for the properties of such a familiar and widely used metal.

The fundamental properties of iron could be accurately determined from metal which contained no trace of any other element but such iron has not yet been prepared, at least in useful quantities. Consequently, its properties have not been determined directly, and there is considerable recent information which indicates that many of the properties of a pure metal cannot be calculated with any degree of certainty by extrapolation to zero impurities of results obtained from a series of impure specimens of graduated composition. There are two serious objections to such extrapolation: (1) The relation between the effect and amount of an added element is seldom linear, especially for high-purity metals, and (2) it is practically impossible to

obtain a series of irons in which there is only one variable in composition.

The effect of the presence of very small amounts of impurities in metals has received increasing attention from metallurgists during the past 15 or 20 years. Metals usually are produced from complex ores which contain a variety of constituents both metallic and non-metallic. The separation of a single metal from such a heterogeneous mass is a difficult problem, particularly from the standpoints of economic operation and quantity production. It has long been known that certain properties of certain metals, for example, the ductility and electric conductivity of copper or the ductility of gold, were appreciably affected by the presence of a few hundredths of 1 per cent, or even by smaller amounts, of certain impurities. Such cases, however, were regarded as exceptions, and in general any common metal which contained 1 per cent or less of total impurities was considered to be satisfactorily pure. It is only in recent years that the production of zinc, aluminum, and lead in states of purity previously not obtainable has demonstrated that the elimination of apparently insignificant amounts of impurities may alter the properties of common metals to such an extent that the pure metal appears to be a new product rather than an improved one. The production of aluminum foil and the successful development of zinc and zinc-base alloys for die casting resulted from the changed properties exhibited by these purified metals. In the case of iron the extraordinary magnetic permeabilities obtained in recent years on a few samples are the result, at least in part, of increased purification of the specimens. The present belief is quite general, that no fundamental property of any metal can be stated with certainty, or with precision, unless it has been determined from specimens of the pure metal.

The need for reliable fundamental data for iron has developed as a result of the demand for new and improved properties in plain and alloy steels, to meet requirements of constantly increasing severity in metallurgical and engineering service. Alloys to meet these new requirements have been developed largely by "cut and try" methods. At least 12 metallic elements, aluminum, chromium, cobalt, copper, manganese, molybdenum, nickel, silicon, titanium, tungsten, vanadium, and zirconium have been added singly or in combination to iron which already con-

tained more or less carbon, silicon, manganese, sulphur, phosphorus, and perhaps other constituents, in the hope that the resulting heterogeneous mixture would have the desired property or combination of properties. If accurate data were available in regard to the fundamental properties of iron itself and the effect of added elements on these fundamental properties, it should be possible, at least to some extent, to substitute calculation for hit-or-miss experimentation in the determination of properties of new alloy combinations or in the determination of the optimum benefit which can be obtained through addition of one or a combination of alloying elements. Certainly the starting point for any such exact knowledge is the determination of the fundamental properties of pure iron.

The literature abounds in references to the properties of this or that specimen of "pure" iron but these claims of ultimate purity cannot be substantiated. In some cases the "pure iron" was commercially pure ingot iron. For several years "electrolytic iron" and "pure iron" were used interchangeably in metallurgical discussions, *i.e.*, any iron produced by any process of electrodeposition was *per se* pure iron; no analysis was necessary. Confirmatory evidence likewise was considered unnecessary in the case of "pure" irons produced by other methods; a recital of the precautions observed in the process was assumed to guarantee the purity of the product. When chemical or spectrochemical analyses have been made, they have seldom, if ever, considered all of the impurities which we now know may be present. Many of these irons deserve to be classed as high-purity irons; some of them *may* have been pure irons but this cannot be demonstrated, and even the purest irons did not agree in properties or behavior.

The determination of purity in a high-purity metal, one which approaches absolute purity, is in itself a major problem. The limits of use of chemical analysis are reached when the purity of the metal is comparable to the purity of the analytical reagents. Spectrochemical analysis is exceedingly useful for the detection of certain elements but unfortunately the sensitivity is not uniform for all elements, in fact, the spectroscope is relatively insensitive to oxygen and carbon, two of the important impurities in iron. Determinations of various physical properties including thermal electromotive force, resistivity, temperature coefficient

of resistivity, magnetic permeability, temperature and sharpness of the allotropic transformations have been proposed as criteria of purity but the value of these determinations, as reliable indications of purity, has not been established.

These considerations perhaps explain the uncertainty which exists in regard to the fundamental properties of iron and justify the authors' attempt throughout the text to refer to high-purity iron and its properties, rather than to pure iron.

In the selection of material for the ensuing discussion of the properties of high-purity iron, the authors attempted to apply two criteria, (1) purity of the material and (2) precision and reliability of the determination. Data which satisfactorily conform to both criteria are relatively few; in many cases either the purity of material or the precision of the determination cannot be defined; frequently the best available data were obtained from irons of commercial purity. Some data which the authors consider to be of doubtful value have been included for two reasons, to complete the review of available information and because the authors' opinion is not infallible in evaluating these reported results. In some instances it has been possible to supplement results obtained from the literature with hitherto unpublished information.

STRUCTURE OF HIGH-PURITY IRON

Crystal Form—Allotropy—Microstructure—Authors' Summary

A study of the structure of a metal includes determinations of the crystal form, of allotropic transformations and the conditions under which they occur, and of the microstructural features both usual and unusual.

A. CRYSTAL FORM

Opinions of early investigators differed regarding the nomenclature to describe the appearance of crystals of iron. Peligot[3] in 1844 considered the crystals to be octahedra. Prior to 1864, Wöhler, Miller, and Fuchs found that iron crystallized in the cubic system, according to Stead.[82]

By about 1890 it was generally agreed that iron crystallizes in the cubic or isometric system. Linck[67] in 1893 observed that octahedral or cubic faces, or both, might be present. Andrews[63] measured the angles of crystal faces in "practically pure wrought iron" and found them to be about 120°. In 1898 Stead[82] stated that "by strongly etching pure iron, square crystals apparently in the form of flat plates are developed, confirming what is universally acknowledged, that iron crystallizes in the cubic system." Osmond[96] in 1900 reviewed the previous work and concluded that "iron in its three states crystallizes in the cubic system, gamma iron generally in octahedra more or less imperfect, beta and alpha iron in cubes." Kahlbaum[87] reported that cubic crystals predominated in iron prepared by distillation, but that octahedra were present.

Osmond and Cartaud[105] investigated the crystal structure of iron by a procedure involving the reduction of ferrous chloride by hydrogen at 650 and 810°C., and by zinc vapor at 1000°C., with formation of crystals in the alpha-, beta-, and gamma-iron ranges. Both alpha and beta iron crystallized in the form of cubes with frequent modifications of the edges; the crystalline

form of gamma iron consisted of combinations of the cube and the octahedron derived from the cube. It was suggested that the crystals which Peligot[3] produced by a similar process and considered to be octahedra were actually cubes with pyramidal ends. Results of a study of deformation figures, crystalline figures, segregation figures, and twinning in alpha and gamma iron were summarized by Osmond and Cartaud[148] as follows:

Properties	Alpha iron	Gamma iron
Planes of translation..........	(1 1 1)	(1 1 1)
Folds......................	Dominant	Absent
Planes of mechanical twinning..	(1 1 1)	(1 1 1)
Planes of twinning by annealing	None	(1 1 1)
Face of maximum hardness.....	(1 1 1)	(0 1 1)
Planes of easiest etching......	(0 0 1)	(0 0 1)

X-ray spectrographic investigations subsequently confirmed the belief, based on visual crystallographic examination, that the forms of iron which are stable at relatively low temperatures crystallize in the cubic system, and extended the range of knowledge to include the crystal structure of iron at higher temperatures. These X-ray investigations are discussed below.

48. Lattice Constants.— The first investigation of the crystal structure of iron by X-ray methods was that of Hull[374,375,403] in 1917 to 1919. He used iron powder which was prepared by reduction of iron oxide with hydrogen and concluded that the space lattice of alpha iron was a body-centered cube with an edge length of 2.86 Ångström units at room temperature. Wever[457] obtained somewhat lower values, 2.848 and 2.849 Å., respectively, for the lattice constants of electrolytic iron and of Kahlbaum reduced iron, but subsequently[687] reported the value 2.863 Å. for electrolytic iron at room temperature.

X-ray methods for the determination of the crystal structure of iron at elevated temperatures were first used by Westgren.[456] At 800°C. he found the space lattice to be a body-centered cube with a lattice constant of 2.92 Å. This agrees closely with the theoretical value for alpha iron at that temperature, based on Westgren's value of 2.83 Å. for alpha iron at room temperature, and the coefficient of thermal expansion of iron. From this

Westgren concluded that beta iron does not exist as an independent modification. Gamma iron was found to have a face-centered cubic lattice with an edge length of 3.60 Å. at 1000°C. Westgren and Phragmén[493] extended the investigation to include delta iron whose structure was found to be the same as that of alpha iron, a body-centered cube. With refined methods new values were obtained for the lattice constant a as follows:

Material	a
Alpha iron at 16°C.	2.87 Å.
Alpha iron at 800°C.	2.90 Å.
Gamma iron at 1100°C.	3.63 Å.
Delta iron at 1425°C.	2.93 Å.

The X-ray photograph of delta iron contained interfering gamma-iron lines, but Westgren and Phragmén modified their apparatus and subsequently[586] obtained a photogram free from interferences which confirmed the fact that the structure of delta iron was the same as that of alpha iron.

Owen and Preston[483] reported 2.869 Å. as the lattice constant of alpha iron at room temperature; McKeehan[523] gave the constant as 2.872 Å. Davey[551] in 1924 reported 2.861 Å. for "chemically pure" iron and in the following year[602] obtained values of 2.858 Å. for hydrogen-reduced iron and 2.855 Å. for electrolytic iron. Wyckoff and Crittenden[645] determined the space lattice of iron prepared by reduction of pure magnetite with nitrogen-hydrogen mixtures. The average of six determinations at room temperature was 2.859 ± 0.004 Å. Eisenhut and Kaupp[773] obtained the value 2.863 Å. on similar material. Brill and Mark,[768] in the course of an X-ray investigation of the decomposition of iron cyanides, determined the lattice constant of the end product, alpha iron, to be 2.863 Å. Osawa[680] gave 2.865 Å. as the value for Armco iron at 15°C.

Precision measurements by the powder method were made by Blake[595] on iron which was stated to contain some carbon. Results on this iron were checked against those on Burgess' electrolytic iron with good agreement. Blake's photograms, corrected for film shrinkage and penetration of the sample, gave 2.8603 ± 0.0002 Å. for the lattice constant of alpha iron at room temperature. Mayer[845] obtained the value 2.861 ± 0.0003 Å. as an average of determinations on forty specimens of iron prepared from iron carbonyl. Mayer ascribed the difference

between his result and that of Blake to the probable use of different values for the lattice constant of sodium chloride which both investigators used in calibrating their apparatus. Recent determinations are 2.8607 ± 0.0002 Å. for "very pure iron," by Owen and Yates,[1020] and 2.8604 Å. for vacuum-melted electrolytic iron, by Jette and Greiner.[1007]

TABLE 6.—LATTICE CONSTANTS OF HIGH-PURITY IRON

Tempera-ture, °C.	Ångström units			
	Esser and Müller[997]			Schmidt[1028]
	Sample 1	Sample 2	Sample 3	
20	2.8611	2.8611	2.8617	2.8611
100	2.8640	2.8648	2.8648	2.8637
200	2.8683	2.8692	2.8689	2.8672
300	2.8727	2.8739	2.8735	2.8706
400	2.8780	2.8785	2.8784	2.8743
500	2.8828	2.8826	2.8824	2.8779
600	2.8877	2.8879	2.8884	2.8816
700	2.8929	2.8927	2.8935	2.8854
750	2.8945	2.8940	2.8950	2.8874
800	2.8974	2.8974	2.8972	2.8897
850	2.8997	2.8986	2.8985	2.8924
870	. . . . . .	. . . . . .	2.8995	
875	2.9008	. . . . . .	. . . . . .	2.8942
880	. . . . . .	. . . . . .	2.9003	
890	. . . . . .	. . . . . .	. . . . . .	2.8953
900	3.6423	3.6460	3.6447	3.636
1000	3.6520	3.6559	3.6541	3.645
1100	3.6598	3.6669	3.6628	3.654
1200	. . . . . .	. . . . . .	. . . . . .	3.662
1300	. . . . . .	. . . . . .	. . . . . .	3.671
1400	. . . . . .	. . . . . .	. . . . . .	3.680
1400	. . . . . .	. . . . . .	. . . . . .	2.925
1435	. . . . . .	. . . . . .	. . . . . .	2.927

Unpublished results obtained by Jette and Foote included the following: 2.8604 for carbonyl iron of German origin; 2.8607 for Merck's iron which had been treated for 15 hr. in dry hydrogen at 500°C.; 2.8607 for a sample of carbonyl iron which had been treated for 24 hr. in dry hydrogen at 1490°C.; and 2.8605

for a sample of ingot iron which had been treated for 18 hr. in moist hydrogen at 1500°C. The first and last of these four results have been corrected for the effect of impurities known to be present.

The effect of temperature on the lattice constant of iron was studied by Bach,[816] Esser and Müller,[997] and Schmidt.[1028]
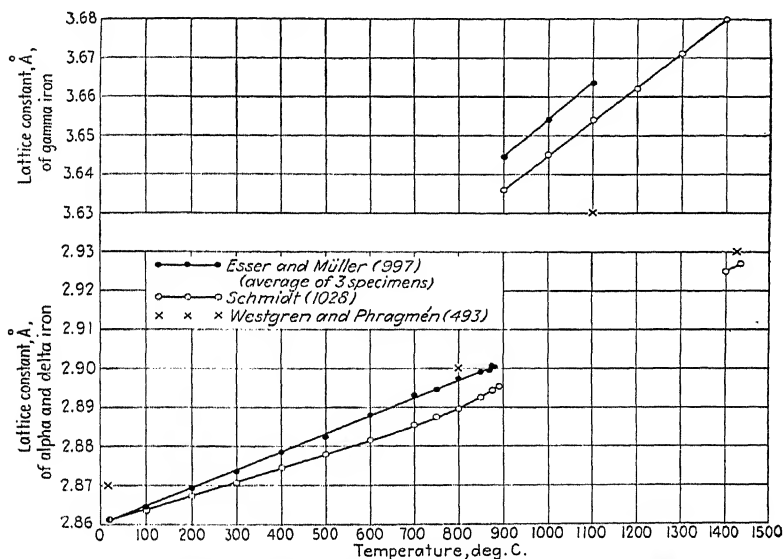
FIG. 5.—Variation of the lattice constant of iron with temperature.

Bach's limited data indicated a pronounced contraction in the lattice at the A_2 point, but this discontinuity has not been confirmed. Esser and Müller used three specimens: No. 1, electrolytic iron containing 0.01 per cent of carbon; No. 2, also electrolytic iron but containing 0.04 per cent of carbon; No. 3, carbonyl iron containing only a trace of carbon. Similar results were obtained for all three specimens throughout the range of temperatures in which alpha iron exists, but in the gamma field slightly higher results were consistently obtained from the carbonyl iron. Schmidt also used electrolytic iron. Data from these two investigations are given in Table 6, the numerical

data ascribed to Schmidt being derived for even temperatures from his plotted results. Figure 5 is a graphic presentation of the data of Esser and Müller and of Schmidt, with the four determinations of Westgren and Phragmén[493] also shown. The data indicate that the lattice dimensions of alpha, gamma, and delta iron increase regularly with increasing temperature, in the range of temperatures in which each form of iron is stable. There is a marked increase in lattice constant accompanying the transformation from alpha to gamma iron, with a roughly equivalent decrease accompanying the transformation of gamma to delta iron. The few points which represent the limited data for delta iron lie approximately on an extension of the curve for alpha iron.

49. Summary of Crystal Form of Iron. The results of X-ray spectrographic investigations have demonstrated that alpha and delta iron have identical crystallographic structure, that of body-centered cubes, while gamma iron has a face-centered cubic structure. The recent investigations of Mayer,[845] Esser and Müller,[997] Schmidt,[1028] Owen and Yates,[1020] and Jette and Greiner[1007] agree on the value 2.861 Å. as the lattice constant of alpha iron at 20°C. Hull[375] in 1917 gave 2.86 Å. for this constant, an indication of the precision of his work.

The agreement between the values of the various investigators for the lattice constant at elevated temperatures is not entirely satisfactory. The values of Esser and Müller for alpha iron are intermediate between the values of Schmidt and those of Bach[816] and Westgren and Phragmén.[493] On the other hand, Schmidt's values for gamma iron are intermediate between the values obtained by other investigators. For delta iron only a limited number of determinations have been reported, constituting an approximate extension of the curve for alpha iron.

At the alpha-gamma transformation, somewhat above 900°C., the body-centered cubic lattice of alpha iron, with an edge length of 2.90 Å., changes to a face-centered cube with an edge length of about 3.64 Å. The lattice constant of gamma iron increases with increasing temperature to 3.68 Å. at the gamma-delta transformation at about 1400°C. At this temperature the face-centered cubic structure of gamma iron reverts to the body-centered structure of delta iron with a lattice constant of about

2.92 Å. The structure of delta iron is that of a body-centered cube at all temperatures up to the melting point.

B. ALLOTROPY

Allotropy is the capacity of a material to undergo a change in the crystal structure, accompanied by a reversible change in many of its physical properties.

50. Historical Review.—According to Osmond[48] the first reference in the literature to an anomaly in the properties of iron was that of Gilbert who in 1600 discovered the loss in magnetism which occurred when a magnet was heated to redness. Benedicks[250] credited Angerstein with first calling attention, in 1778, to the recalescence in steel during cooling. The sudden elongation of an iron wire, cooling from a red heat, was observed by Gore[20] in 1869 and was confirmed in 1873 by Barrett[25] who also detected a sudden contraction during heating, and recalescence during cooling in the dark.

According to Benedicks[254] the first report of Osmond of his classic work on the allotropy of iron was a manuscript presented in 1883 to the Academy of Sciences in Paris, in which was set forth the conclusion that iron exists in two allotropic modifications. Osmond[48] subsequently reported three points of discontinuity in the heating and cooling curves of electrolytic iron, which points he designated by the terms A_1, A_2, and A_3. As the discontinuities were not developed at exactly the same temperatures during heating and cooling, Osmond added the subscript c (chauffage) to signify the point obtained on heating and the subscript r (refroidissement) to indicate the point obtained on cooling. The discontinuity at the lowest temperature, the A_1 point, was correctly ascribed by Osmond to the presence of carbon (0.08 per cent). In modern language the A_1 discontinuity occurs at the temperature of the eutectoid between iron and iron carbide and does not represent an allotropic change in the iron itself. There would be no discontinuity at the A_1 point in pure, carbon-free iron.

Osmond found that the Ac_2 point occurred between 710 and 730°C., the Ar_2 point between 750 and 690°C. The third discontinuity, the A_3 point, also covered a considerable range of temperatures from 840 to 900°C. on heating, but was sharply

defined at 855°C. on cooling. (The temperatures reported by Osmond were in error due to the low temperature assumed for the melting point of potassium sulphate which was used in the calibration of his thermocouples. About 50°C. should be added to the temperatures reported by Osmond, in the temperature range of approximately 900°C.). Osmond considered it probable that the A_2 point was the end of the A_3 point, retarded by the presence of carbon, and concluded that "iron below Ar_2 possesses the molecular form alpha, and assumes above Ar_3 the allotropic form beta. Between Ar_2 and Ar_3, when these two points are distinct, the metal is a mixture of the two varieties alpha and beta." Absence of indications of A_2 on cooling curves made by Roberts-Austen[54] on electrolytic iron containing 0.007 per cent of carbon lent support to the belief that the A_2 point was an effect of the carbon in Osmond's iron. Later, however, Osmond[58] found that the A_2 point coincided with the magnetic transformation and concluded that A_2 and A_3 were separate points. Iron, therefore, existed in three modifications, alpha, beta, and gamma. Arnold[61] expressed doubt that iron has allotropic modifications, ascribing the discontinuities to the presence of impurities, particularly carbon and sulphur. In a discussion of Arnold's paper, Osmond cited the discontinuities in thermal expansion, electric resistance, magnetic susceptibility, and thermoelectric power observed at A_3 by other investigators as evidence that the point represented an allotropic transformation. The investigation by Curie[62,64] in 1894 on the effect of temperature on the magnetic properties of iron showed the A_2 and A_3 points to be separate, independent points and in addition revealed a third point, the A_4 transformation which, owing to the faulty pyrometry of the time, was placed at 1280°C. Previously, Ball[47] in the course of an investigation of the effect of temperature on the tensile properties of iron, had found indications of a discontinuity at a temperature estimated by him as 1300°C. That A_2 was a separate point in high-purity iron and not an effect of impurities was confirmed by Roberts-Austen in 1895[67] and 1899,[90] by cooling curves on electrolytic iron.

The investigations of Osmond[96] in 1900 and Osmond and Cartaud[105] in 1901 on the crystal structure of iron demonstrated that alpha and beta iron are alike in crystal form but are different

TABLE 7.—TEMPERATURE OF THE A_2 TRANSFORMATION

Investigator	Date	Material	Temperature, °C.		
			Ac_2	A_2	Ar_2
Thermal analysis					
Carpenter and Keeling[121]	1904	Swedish iron			762
Harkort[157]	1907	Swedish iron	755 to 762		762 to 756
Müller[196]	1909	Electrolytic iron	770		763
Carpenter[276]	1913	Electrolytic iron			768 to 741
Burgess and Crowe[275]	1913	Electrolytic iron	768		768
Guillet and Portevin[282]	1913	Electrolytic iron	788		778
Sauveur[294]	1913	Electrolytic iron	769		725
Sauveur[314]	1914	Electrolytic iron	765		759
Ruer and Goerens[236]	1915	Electrolytic iron	769		769
Sanfourche[393]	1918	Hydrogen-reduced iron	765		746
Tritton and Hanson[585]	1924	Electrolytic iron	763		763
Ruer and Bode[629]	1925	Electrolytic iron	769		769
Wever[750]	1927	Electrolytic iron			768
Calorimetric methods					
Harker[131]	1905	Soft iron		825	
Weiss and Beck[187]	1908	Electrolytic iron		758	
Meuthen[262]	1912	Electrolytic iron		770 to 790	
Laschtschenko[308]	1914	Electrolytic iron		730	
Weiss, Piccard, and Carrard[350]	1916	Electrolytic iron		784	
Wüst, Meuthen, and Durrer[395]	1918	Electrolytic iron		725 to 785	
Klinkhardt[725]	1927	Electrolytic iron		780 to 785	
Oberhoffer and Grosse[735]	1927	Electrolytic iron		785	
Umino[745]	1927	Electrolytic iron		820	
Dilatometric methods					
Benedicks[297]	1914	Electrolytic iron		767	
Chevenard[366]	1917	Electrolytic iron		760	
Chevenard[702]	1927	Electrolytic iron		765	
Electric-resistance methods					
Morris[75]	1897	Charcoal iron		765	
Meyer[246]	1911	Kahlbaum iron		700	
Meyer[246]	1911	Armco iron		700	
Meyer[246]	1911	Electrolytic iron		710	
Broniewski[271]	1913	Electrolytic iron		750 to 850	
Honda and Ogura[306]	1914	Kahlbaum iron		810	
Burgess and Kellberg[326]	1915	Electrolytic iron		757	
Saldau[355]	1916	Kahlbaum iron		780	
Saldau[355]	1916	Electrolytic iron		780	
Iitaka[389]	1918			790	
Magnetometric methods					
Curie[62,64]	1894	Soft iron		750	
Morris[75]	1897	Swedish iron		770	
Weiss and Beck[187]	1908			753	
Terry[225]	1910	Electrolytic iron		785	
Honda and Takagi[242]	1911	Kahlbaum iron		770	
Honda and Takagi[243]	1912	Kahlbaum iron		810	
Weiss and Foëx[250]	1911	Electrolytic iron		774	
Ruer and Kaneko[311]	1914			769	
Yensen[321]	1914	Electrolytic iron		785	
Ruer and Bode[629]	1925	Electrolytic iron		769	
Regner[903]	1930	Electrolytic iron		767 to 762	
Thermoelectric methods					
Broniewski[271]	1913	Electrolytic iron		730	
Burgess and Scott[348]	1916	Electrolytic iron		768	
Berliner[498]	1923	Electrolytic iron		768	
Galibourg[611]	1925	Electrolytic iron		780	

from gamma iron. Stead and Carpenter,[295] from a study of the recrystallization of electrolytic iron during annealing, also concluded that there is no crystallographic difference between alpha and beta iron.

An additional method for identification of the transformations of metals was described recently by Hayakawa.[1002] He found that irregularities occurred, at the A_2 and A_3 points of iron, in the rate of emission of secondary electrons which are excited by a thermionic current but his results appear to be of qualitative rather than of quantitative value for identification of the A_2 and A_3 temperatures.

51. The A_2 Point. In view of the readily demonstrable discontinuities in the properties of iron and the change in crystal structure observed at A_3, it was generally accepted that iron undergoes an allotropic modification at this point. At the A_2 point, however, no crystallographic change was detectable and only the magnetic properties show a marked anomaly. This difference between the A_2 and A_3 points resulted in a long controversy regarding the nature of A_2 and the existence or non-existence of beta iron as a separate allotropic form. Among the more important papers containing material on the subject are those by Rosenhain and Humfrey,[2204] Benedicks,[254,255] Carpenter,[276] Sauveur,[294,314] Honda and coworkers,[242,283A,330A,331,401] Burgess and associates,[275,326,348] and Ruer and coworkers.[336,629] A review of this controversial literature would hardly be profitable now, inasmuch as the X-ray work of Westgren[456] and others has demonstrated that no crystallographic change occurs in iron below the A_3 point. The change at the A_2 point, according to Honda,[330A] is not an allotropic transformation but is an intermolecular change related to the loss of magnetism. The results of Burgess and Crowe,[275] Ruer and Goerens,[336] Tritton and Hanson,[585] and Ruer and Bode[629] indicate that A_2 occurs at the same temperature on heating and on cooling without hysteresis.

The temperatures which have been reported for the A_2 point are given in Table 7.

Averages of the results which have been reported since 1910 for determinations of the A_2 point, including the numerical average of the Ac_2 and Ar_2 values determined by thermal analyses, are as follows:

Method	A_2, °C.
Thermal analysis	765
Calorimetric methods	777
Dilatometric methods	764
Electric-resistance methods	759
Magnetometric methods	780

Av. 769 (1416°F.)

52. The A_3 Point.—The A_3 point is the temperature below which iron exists in the alpha form, and above which it exists in the gamma form. The alpha-gamma transformation exhibits the hysteresis which is characteristic of many allotropic transformations, the change occurring at a lower temperature upon cooling than upon heating. The temperature range between the Ac_3 and Ar_3 points decreases with decreasing rate of heating and, for very pure material with very slow heating and cooling, there is only a slight difference between the Ac_3 and Ar_3 temperatures. Austin and Pierce[1046] and Mehl[1080] have found that specimens of hydrogen-treated carbonyl iron had a hysteresis of but 1 or 2°C., when heated and cooled at slow rates. However, it is only in the most recent investigations that this lack of hysteresis has been obtained. In the earlier reports there is invariably a considerable difference between the Ac_3 and Ar_3 temperatures.

The results reported for the temperature of the A_3 transformation are given in Table 8.

In order to arrive at a figure representative of the most probable value for the A_3 transformation in iron, the data of Table 8 have been critically reviewed. Data obtained from iron of completely unknown purity or of known low purity and values representative of but a single unconfirmed determination, or averages of a series which showed a wide spread, were discarded. From the remaining data only those values definitely known to represent the Ac_3 temperature were selected. Determinations of the Ac_3 transformation give a better indication of the temperature of the A_3 point than do determinations of Ar_3. The latter are noticeably affected by the rate of cooling whereas the Ac_3 determinations are affected only slightly by the rate of heating. This was shown by Burgess and Crowe[275] for thermal-analysis methods and, according to Mehl,[1080] by Wells for dilatometric methods.

TABLE 8.—TEMPERATURE OF THE A_3 TRANSFORMATION

Investigator	Date	Material	Temperature, °C.		
			Ac_3	A_3	Ar_3
Thermal analysis					
Roberts-Austen[51]	1891	Electrolytic iron			850
Arnold[61]	1894	Electrolytic iron	885		
Roberts-Austen[67]	1895	Electrolytic iron			895
Carpenter and Keeling[121]	1904	Swedish iron			895
Harkort[157]	1907	Swedish iron	910 to 917		888 to 875
Müller[196]	1909	Electrolytic iron	917*		894
Burgess and Crowe[275]	1913	Electrolytic iron	912*		890
Carpenter[276]	1913	Electrolytic iron	916*		888
Guillet and Portevin[282]	1913	Electrolytic iron	932		902
Sauveur[314]	1914	Electrolytic iron	915*		895
Ruer and Goerens[336]	1915	Electrolytic iron			900
Sanfourche[409A]	1919	Hydrogen reduced iron	959		877
Tritton and Hanson[565]	1924	Electrolytic iron	912*		885
Wever[750]	1927	Electrolytic iron			906
Harrington and Wood[999]	1930	Decarburized Armco iron	865 to 910		902 to 874
Calorimetric methods					
Harker[151]	1905	Soft iron		865	
Oberhoffer[162]	1907	Electrolytic iron		883	
Meuthen[262]	1912	Electrolytic iron		880 to 900	
Laschtschenko[306]	1914	Electrolytic iron		895	
Wüst, Meuthen, and Durrer[306b]	1918	Electrolytic iron		919	
Klinkhardt[725]	1927	Electrolytic iron		906 to 909	
Oberhoffer and Grosse[735]	1927	Electrolytic iron		906	
Umino[745]	1927	Electrolytic iron		900 to 930	
Electric-resistance methods					
Honda and Ogura[306]	1914	Kahlbaum iron		930	
Burgess and Kellberg[326]	1915	Electrolytic iron		894	
Saldau[355]	1916	Kahlbaum iron	940 to 920		920 to 910
Saldau[355]	1916	Electrolytic iron	910*		900
Iitaka[389]	1918		950		910
Magnetometric methods					
Weiss and Foëx[250]	1911	Electrolytic iron		920	
Yensen[321]	1914	Electrolytic iron			894
Honda and Takagi[331]	1915	Electrolytic iron	911*		898
Honda and Takagi[331]	1915	Electrolytic iron	908*		889
Ishiwara[377]	1917	Electrolytic iron		903	
Terry[384]	1917	Electrolytic iron	918*		903
Austin and Pierce[1046]	1934	Vacuum-melted electrolytic iron		938	
Austin and Pierce[1046]	1934	Hydrogen-melted ingot iron		917	
Austin and Pierce[1046]	1934	Hydrogen-treated carbonyl iron		928	

* Designates selected value. See text, pages 105 and 108.

TABLE 8.—TEMPERATURE OF THE A_3 TRANSFORMATION.—(Continued)

Investigator	Date	Material	Temperature, °C.		
			Ac_3	A_3	Ar_3
Dilatometric methods					
Charpy and Grenet[108,109]..	1902	Ingot iron		860 to 890	
Broniewski[271]	1913	Electrolytic iron		890 to 905	
Benedicks[297]	1914	Electrolytic iron		903 to 906	
Chevenard[366]	1917	Electrolytic iron		870	
Souder and Hidnert[490]. . . .	1922	Electrolytic iron	912*		906
Satô[630].	1925	Electrolytic iron	905*		885
Chevenard[767].	1927	Electrolytic iron		900 to 920	
Esser ?	1927	Electrolytic iron	906*		897
Honda and Miura[784]	1928	Armco iron	860 to 895		889 to 850
Hensel and Larsen[1005]. . . .	1933	Hydrogen-treated ingot iron	935		925
Hensel and Larsen[1005]. . . .	1933	Electrolytic iron, vacuum-melted and hydrogen-treated	935		915
Hensel and Larsen[1005]. . . .	1933	Electrolytic iron, hydrogen-melted and hydrogen-treated	921		914
Hensel and Larsen[1005]. . . .	Average	. . . .	930*		911
Austin and Pierce[1046].	1934	Cathode electrolytic iron	890		912
Austin and Pierce[1046].	1934	Electrolytic iron, vacuum-melted	938 to 949		935 to 937
Austin and Pierce[1046].	1934	Electrolytic iron, hydrogen-melted	904 to 906		920 to 911
Austin and Pierce[1046].	1934	Ingot iron, hydrogen-melted	912 to 917		915
Austin and Pierce[1046].	1934	Ingot iron, hydrogen-treated	915		911
Austin and Pierce[1046].	1934	Electrolytic iron, vacuum-melted	930 to 933		927 to 925
Austin and Pierce[1046].	1934	Carbonyl iron, hydrogen-melted	915 to 916		911 to 913
Austin and Pierce[1046].	1934	Carbonyl iron, hydrogen-treated	930		927 to 929
Austin and Pierce[1046].	1934	Carbonyl iron, hydrogen-treated	928		927
Austin and Pierce[1046].	1934	Selected value	929*		927
Thermoelectric methods					
Broniewski[271]	1913	Electrolytic iron		950	
Benedicks[346]	1916	Electrolytic iron		895	
Burgess and Scott[348].	1916	Electrolytic iron	910*		900
Berliner[408].	1923	Electrolytic iron	910*		900
Goetz[561].	1924	Electrolytic iron	910*		900
Galibourg[611]	1925	. . . .	905 to 940		925 to 878
Crystallographic methods					
Stead and Carpenter[295]. . .	1913	Electrolytic iron		900 to 915	
Roberts and Davey[854]. . . .	1929	Purified nitrate, reduced in hydrogen		907 to 910	
Rogers[855]	1929	Electrolytic iron	912*		899
Hydrogen-solubility method					
Sieverts[248]	1911	Kahlbaum iron		900	

* Designates selected value. See text, pages 105 and 108.

These factors limit consideration to the 18 independent determinations indicated by asterisks in Table 8.

A summary of these 18 determinations for Ac_3 is as follows:

Number and Method	Ac_3, °C.
5 by thermal analysis	914
5 by dilatometric methods	916
3 by magnetometric methods	912
3 by thermoelectric methods	910
1 by electric-resistance methods	910
1 by crystallographic methods	912

Av. 912 (1674°F.)

The rounded value 910°C. (1670°F.) is probably the best present approximation of the temperature of the A_3 transformation of iron. The results of Hensel and Larsen and of Austin and Pierce (Table 8) indicate that A_3 in iron of unusual purity may be considerably higher than the average of the reported results. These high values were obtained principally on specimens of hydrogen-treated iron by measurements of thermal expansion although Austin and Pierce also obtained high results on three specimens by measurements of magnetic susceptibility. However, these high values were not confirmed by the results of dilatometric observations which were reported recently from the Metals Research Laboratory of the Carnegie Institute of Technology.[1080] The material which was used in these experiments was carbonyl iron which had been treated with hydrogen at 1200°C. for periods of about 200 hr. Slow rates of heating and cooling were used, which resulted in a spread of only 2 or 3°C., and even of only 1°C., between the Ac and Ar temperatures. The Ac_3 points determined for carbonyl iron, together with the cooling rates used, were reported as follows: 908 ± 2°C. at 2°C. per min.; 907 ± 2°C. at 0.125°C. per min. The Ar_3 determinations were as follows: 904° at 2°C. per min.; 906° at 0.5°C. per min.; 907° at 0.125°C. per min.

It is evident that the spread between the Ac_3 and Ar_3 points can be practically eliminated by the technique and methods which are now available, but further work is necessary to decide whether or not the temperature of the A_3 transformation is appreciably higher for extremely pure iron than for somewhat less pure material.

53. The A_4 Point.—The A_4 point marks the transformation of gamma to delta iron, the range of stability of the latter being from A_4 to the melting point. The X-ray investigation of Westgren and Phragmén[493] showed that delta iron is identical in crystal structure with alpha iron. Little information is available as to the amount of hysteresis at A_4, but it would be expected to be slight because the rate of reaction would be high at the high temperature of the A_4 point. The work of Terry[384] indicated that it is negligible as compared with that at the A_3 point. The temperatures which have been reported for A_4 are given in Table 9.

TABLE 9.—TEMPERATURE OF THE A_4 TRANSFORMATION

Investigator	Date	Material	Temperature, °C. A_4
Thermal analysis			
Harkort[157]............	1907	Swedish iron	1380
Ruer and Kaneko[292]..	1913		1420
Ruer and Klesper[293]..	1913	Electrolytic iron	1401
Ruer and Goerens[336].	1915	Electrolytic iron	1401
Sanfourche[393]........	1918	Hydrogen-reduced iron	1365
Wever[750].	1927	Electrolytic iron	1401
Calorimetric methods			
Wüst, Meuthen, and Durrer[395]....	1918	Electrolytic iron	1404.5
Oberhoffer and Grosse[735]........	1927	Electrolytic iron	1401
Umino[867].....................	1929	Electrolytic iron	1390 to 1410
Dilatometric methods			
Satô[630].....................	1925	Electrolytic iron	1400
Magnetometric methods			
Weiss and Foëx[250]..............	1911	Electrolytic iron	1395
Ishiwara[377]...................	1917	Electrolytic iron	1390
Terry[384].....................	1917	Electrolytic iron	1407
Thermoelectric methods			
Goetz[561].....................	1924	Electrolytic iron	1410 to 1400

Averages of values which have been reported since 1910 are as follows:

Method	A_4, °C.
Thermal analysis	1398
Calorimetric methods	1402
Dilatometric methods	1400
Magnetometric methods	1397
Thermoelectric methods	1405

Av. 1400 (2550°F.)

This average value, 1400°C. (2550°F.), is probably the best present approximation of the temperature of the A_4 point.

54. Other Supposed Transformation Points. Numerous investigators have observed discontinuities at temperatures other than those usually associated with the transformation points of iron and have suggested the possibility of the existence of additional transformations.

Sirovich[532] noted a discontinuity in the thermal expansion of electrolytic iron at 373°C. which he suggested was evidence of a polymorphic transformation. Rawdon, Hidnert, and Tucker[683] pointed out the probability that this was an effect of occluded hydrogen. Dearden and Benedicks[657] found a discontinuity at 250°C. in the magnetization-temperature curve of annealed electrolytic iron. Quenched electrolytic iron gave two points, 225 and 345°C. Anomalies observed by Forrer and Schneider[881] in magnetization curves of electrolytic iron suggested to them the possibility that there are two different types of pure iron stable at ordinary temperatures, one being formed by annealing at 200 to 400°C., the second by annealing at 450 to 900°C.

Goffey and Thompson[510] noted well-defined peaks, at 70, 120, 170, 230, and 310°C., in the coefficient of resistivity-temperature curves of electrolytic iron. Ishimoto,[404] using tuning forks and torsion pendulums of high-purity iron, investigated the number of vibrations necessary to produce a certain degree of damping at different temperatures. Discontinuities at 65, 183, and 260°C. were found during heating; on cooling the points were at 65, 170, and 260°C. Brinell hardness versus temperature curves showed discontinuities at about the same temperatures. Ishimoto's points agree fairly closely with discontinuities found

by Goffey and Thompson[510] in their curves showing the change with temperature of the torsional elastic limit of high-purity iron rods. Borelius and Gunneson[549] heated cathode electrolytic iron in a vacuum at a constant rate and noted the increase in pressure due to emission of occluded gases. The increase in pressure plotted against temperature gave a curve showing accelerated emission at 150, 220, 300, 460, 530, and 600°C. At 730°C. an absorption of gas occurred. Pilling[485] in a similar experiment noted maxima in the rate of emission of occluded gases at 200°C. and between 600 and 700°C. Jaquerod and Gagnebin[835] found that the velocity of diffusion of hydrogen through iron increased suddenly at about 200°C. which agrees with Pilling's result and is near the 220°C. point of Borelius and Gunneson.

The results of determinations of complex mechanical properties, such as hardness and torsion, should not be interpreted in terms of allotropic transformations. In general, the cause of these reported anomalies has not been definitely established for iron. In the case of other metals, zinc for example, it has been shown that anomalies, which were observed for somewhat impure specimens, could not be found in more highly purified material. In the authors' opinion, these minor discontinuities are the result of the presence of impurities and do not represent allotropic transformations. In most cases the specific impurity has not been identified but in at least one case the supposed transformation has been subsequently ascribed to the presence of hydrogen. Attention is called to the fact that many reports have been made of a supposed transformation at 200 to 220°C.; in the modern iron-carbon diagram approximately 215°C. (420°F.) is given as the A_0 point, which is not a transformation point of iron but represents the magnetic change in ·cementite. There is no A_0 point in pure iron.

No allotropic change in iron below 0°C. has ever been observed, according to Heindlhofer.[1056]

55. Summary of the Allotropy of Iron.—Iron has two allotropic transformations and a magnetic transition. The magnetic transition, the A_2 point, marks the change of ferromagnetic iron to paramagnetic iron. Methods such as thermal analysis, which determine the point at which the rate of change is most rapid, place it at about 770°C. (1420°F.). Magnetometric

methods, which determine the temperature at which the change is complete, place the A_2 point about 10°C. higher.   The magnetic transition is without hysteresis, the change occurring at the same temperature on heating and on cooling.

True allotropic transformations occur at the A_3 and A_4 temperatures.   A rounded value of 910°C. (1670°F.) is suggested as the best present approximation for A_3 with the reservation that appreciably higher temperatures have been indicated by some recent investigations.   It has been shown that with increased purity of the iron the difference between the Ac_3 and Ar_3 points at slow rates of heating and cooling decreases to a temperature interval of 1 or 2°C.

It is suggested that the value 1400°C. (2550°F.), which is the average of the reported values, be accepted as the best present approximation of the A_4 point for the gamma-delta transformation.

Anomalies found by some investigators in various properties of iron at temperatures other than those of the A_2, A_3, and A_4 points have suggested to them the possibility of additional transformations in iron.   X-ray investigations have not confirmed these suggestions.   The A_3 and A_4 points in high-purity iron represent definite transformations and A_2 is a magnetic transition point.   Other reported transformation points presumably were the result of the presence of impurities in the iron or of the determination of complex properties which should not be interpreted in terms of allotropic transformations.

C. MICROSTRUCTURE

The normal microstructure of alpha iron or ferrite is that characteristic of pure metals in general—allotriomorphic crystals in the form of crystalline grains, the appearance of which is familiar to metallurgists and requires no comment.   A great variety of structures may be obtained in cathode iron by varying the factors such as current density, temperature, circulation of solution, composition of electrolyte, gases and impurities in the electrolyte, and thickness of the deposit.   The influence of these factors on surface defects such as treeing, pitting, channelling or grooving has been considered in connection with the electrolytic preparation of iron.   This section is concerned only with the internal structure of the deposited iron.

56. Structure of Electrolytic Iron.—A study of the structure of cathode deposits by Burgess and Watts[142] showed that in the early stages of deposition the structure was fibrous, but with increasing thickness of deposit conical growths formed, the diameter of the cone increasing with continuing deposition. The bases of the cones were slightly rounded nodules which gave the surface of the deposit a blistered appearance. If the nodular deposits were given a sharp blow with a hammer, some of the conical-shaped growths were separated from the deposit leaving conical cavities in the iron. Magnification of 20 diameters of a polished and etched section of a nodule revealed a laminated structure, but at 250 diameters the structure was characteristic of that of ferrite, the grain boundaries being clearly visible. No differing orientation of the crystals, which in normal ferrite is revealed by light and dark patches, was apparent. Upon heating the specimen to 1000°C. the normal ferrite structure with different orientation of crystals was obtained. Burgess and Watts pointed out the similarity between the conical structure of the electrodeposited iron and that of certain minerals such as manganite, hematite, and limonite.

An investigation by Storey[317] was made primarily to determine the effect of annealing on the structure of electrolytic iron. Three general types of structure were observed in the cathode iron prior to annealing, the nodular structure reported by Burgess and Watts, a fine-grained structure, more fibrous than the nodular structure, and a coarse, porous crystalline deposit. Lines parallel to the starting cathode, indicating surfaces of cleavage, were due to some interruption or change in the deposition. The different layers were of variable structure, some being dense and hard while others were porous. Storey noted that in the case of metals solidifying from the molten state the crystals, starting from nuclei, can grow outwards in all directions, which results usually in different orientation in neighboring crystals. On the other hand, in electrodeposition the crystals can grow initially in but one direction—perpendicular to the cathode sheet. Several photomicrographs by Storey revealed the increase in grain size with increasing thickness of deposit. A section next to the cathode sheet and parallel to it showed no crystal grains at 100 diameters magnification, although at higher magnifications grains were discernible. In a cross section

through the middle of the deposit the grains were easily discernible at 100 diameters while on the outside of the deposit the grains were of considerable size. The same grain-size relation was shown by cross sections perpendicular to the cathode. Storey also noted the spider-web appearance of some crystals, first reported by Müller.[196]

Hughes[474] distinguished between two types of structure in electrolytic iron which he denoted by the petrological terms, idiomorphic structure, resulting when the crystals composing the metal have had the opportunity to develop their external forms freely, and hyp-idiomorphic structure, resulting from the fact that the component crystals have not had the opportunity to develop their forms and edges freely but have been compelled to take their shapes from their surroundings. In the early stages of deposition the electrolyte was acid, and iron deposited in a finely crystalline or fibrous structure. As deposition continued there was a gradual change to a normal or coarsely crystalline structure, developing with further deposition into the hyp-idiomorphic structure and finally into the idiomorphic structure at the surface of the deposit. Hughes associated these changes with decreasing acidity of the electrolyte during deposition.

Hughes also noted,[438] in photomicrographs of etched sections of electrodeposited iron, wave-like lines or markings running through the mass of metal, sometimes in herring-bone arrangement on individual grains. He suggested that these lines were slip lines produced in the grains of the metal by the forces of contraction acting during its formation. Abrupt changes in direction of these lines within individual crystals indicated twinning.

57. Factors Affecting the Structure of Electrolytic Iron.—Two characteristic types of structure, the normal (Fig. 6) and the fibrous (Fig. 7), were found in electrolytic iron deposited from the Fischer-Langbein bath. In the normal structure all grains consist of cones with thin solid angles toward the cathode sheet. The true normal structure does not occur; deposits approximate it more or less closely under certain conditions of deposition, namely, a neutral electrolyte and absence of motion in the electrolyte. The degree of approach to the normal structure is affected to some extent by temperature, current density,

concentration, absence or presence of floating matter, and other factors. The fibrous types of structure in longitudinal

Fig. 6.—Conical structure in cathode electrolytic iron. Etched with 2 per cent alcoholic nitric acid. 150 ×. (*Hughes.*[471])

section appeared to be composed of a mass of threads or fibers at right angles to the cathode. This type of structure was
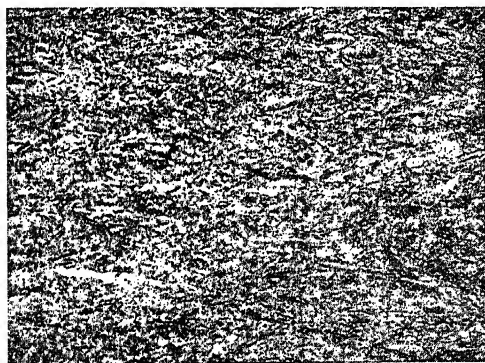
Fig. 7.—Fibrous structure in cathode electrolytic iron. Etched with 5 per cent alcoholic picric acid. 100 ×. (*Thomas and Blum.*[911])

characteristic of deposits formed in a well-agitated solution. Hughes considered constancy of concentration of iron ions at

the cathode, resulting from agitation of the solution, to be one of the requisites for formation of the fibrous structure, the other requisite being the presence of free acid in the electrolyte.

It was pointed out by Blum and Rawdon[[595.4]] that the process of crystal growth in general consists in (*a*) the formation of nuclei, that is, of new crystals and (*b*) the growth of existing crystals. Although the actual constitution of the crystal nuclei could not be defined, it was concluded that the formation of nuclei, or of new crystals, in electrodeposition must be fostered by all factors which increase the difference in potential between the cathode and the solution. These factors include the following: (*a*) increasing the current density and (*b*) decreasing the actual or effective metal-ion concentration in the solution adjacent to the cathode as a result of (1) diluting or (2) cooling the solution, (3) adding a salt with a common ion, (4) adding a substance such as a colloid which hinders the processes of diffusion in the cathode film, (5) increasing the viscosity, (6) forming complex ions. Typical structures of electrodeposited metals were classified into three major groups:

1. All (or practically all) of the initial nuclei continue to grow.
2. Only a part of the initial nuclei continues to grow.
3. None of the initial nuclei continues to grow.

It was shown that the fibrous, columnar, conical, and broken crystals of electrodeposited iron could be explained according to this classification and its subdivisions. Likewise, the size of the crystals and the phenomena of treeing and of twinning in electrodeposits could be explained. Aububert[[543]] also discussed the effect of the relative velocities of crystal growth and of nuclei formation on the structure of electrodeposited metals. A paper by MacFadyen[[406]] on the building up of worn metal parts by electrodeposition of iron was illustrated with several photomicrographs of the different types of structure obtained under different conditions of deposition.

Glocker and Kaupp[[559]] determined the orientation of the crystals in fibrous deposits of electrolytic iron, by means of X-ray. The axis of the fibers was found to be in the [1 1 1] or the [1 1 2] direction depending upon the iron salt used in the electrolyte; it was always in the direction of maximum velocity of growth of the crystal in the solution. Further results on the determination of crystal orientation in films of electrolytic

iron were reported by Bozorth.[596]   For iron the (1 1 1) planes tended to be parallel to the surface.   The results indicated to Bozorth that the special orientation obtained was intimately connected with the stresses which Kohlschütter and Vuilleumier[391] have shown are present in electrodeposited iron.

58. Veining and Network Structures in Alpha Iron.—Certain unusual structures in the ferrite crystals in various types of iron have been discussed in the literature.   Andrews[63] observed a "substructure" in the ferrite grains of wrought iron and termed it "duplex crystallization."   Robin[264] also described this network existing within the ferrite grains.   Storey[317] observed the presence of "inner grains" in the ferrite grains of remelted electrolytic iron.   Storey's explanation of this phenomenon was as follows:

The inner grains are probably groups of similarly oriented iron crystals.   The orientation of all of these groups is alike through the ferrite grain.   In slowly cooling from the molten state large gamma grains are formed.   In changing from the gamma state to the non-gamma state the grain size remains the same.   If we consider that, owing to the large gamma grains, a large number of non-gamma nuclei were formed in each gamma grain and that each nucleus was similarly oriented owing to similarly orientated gamma crystals, we can readily see that the ferrite grains would be composed of a large number of groups of similarly oriented crystals.   These groups of crystals would constitute the inner grains.

Tritton[743] split longitudinally one of the ferrite grains in remelted electrolytic iron and found it to be composed of columnar subcrystals.   The slip lines, formed when the crystal was strained, ran across the numerous subboundaries in straight lines indicating similar orientation in the subcrystals.

A study of unusual features in the structure of ferrite was made by Rawdon and Berglund.[738]   They found that alpha veining, a phantom structure which appears on the surface of certain crystals of ferrite, was a common occurrence in electrolytic iron and open-hearth iron.   Stronger etching than is usual was necessary to reveal its presence, which may account for its infrequent observance elsewhere.   That alpha veining, illustrated in Fig. 8, is not merely a surface marking but continues through the body of the crystal was shown by regrinding, polishing, and etching a marked spot on a specimen.   After removal of considerable metal the same veining pattern was obtained as before

the regrinding.   Alpha veining was not observed in electrolytic
iron as deposited but was found in this material after annealing
at a temperature above the A_3 point.   Ferrite worked at or just
below A_3 showed alpha veining in abundance, but the same
material worked at a very high temperature usually showed
very little.   More drastic etching was required to reveal veining
in quenched ferrite than in the slowly cooled material.   Inclu-
sions often served as centers at which veining started but the
presence of inclusions did not appear to be necessary for its
formation.   There was no indication that the presence of alpha
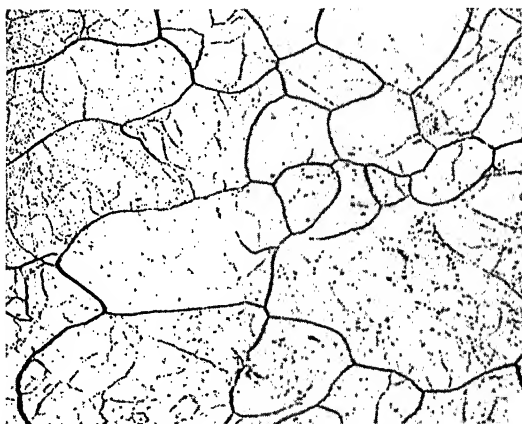
FIG. 8.—Alpha veining in electrolytic iron.   Etched with 5 per cent alcoholic
picric acid.   100×.   (*Rawdon and Berglund.*[738])

veining had any appreciable effect on the mechanical properties
of the metal.   That it is associated with the alpha-gamma
transformation was indicated by the fact that silicon-containing
ferrite, which has no transformation, showed little evidence
of veining.

The dependence of alpha veining on the allotropic transforma-
tion was confirmed by Ammermann and Kornfeld.[814]   Some
of their results on electrolytic iron (not remelted) are as shown on
page 119.   Mechanical deformation at temperatures below the A_3
point did not cause veining in ferrite previously free from it, but if
veining was present mechanical deformation accentuated the con-
dition.   Hanemann, Schrader, and Tangerding[970] found that

Treatment	Structural condition	Conclusion
Air cooled from gamma state (above A_3)	Veining within ferrite grains	Ferrite free from alpha veining can be obtained by cold working and heating below A_3 to permit recrystallization.
Reduced 10 per cent by compression (cold), heated 1 hr. at 750°C. (1380°F.)	Recrystallized, large grains, no veining	
Reduced 10 per cent by compression (cold), heated 1 hr. at 850°C. (1560°F.), then 1 hr. at 880°C. (1615°F.)	No veining after heating to 850°C. No veining after heating to 880°C.	Ferrite free from veining shows no veining after being heated just below A_3.
Reduced 10 per cent by compression (cold), heated 1 hr. at 850°C. (1560°F.), then 1 hr. at 910°C. (1670°F.)	Veining within ferrite grains.	Ferrite free from veining shows veining after being heated just above A_3.

veining occurs at the boundaries of grains which have passed through the gamma-alpha transformation, and at the slip planes of grains which have been annealed after being cold worked. They suggested that it was thus possible to determine whether a piece of iron had been worked at temperatures above the gamma-alpha transformation or had been cold worked.

The primary causes and the conditions necessary for the formation of alpha veining are still controversial matters. Ammermann and Kornfeld[990] believed that it was due not to the presence of impurities but primarily to passage through the gamma-alpha transformation, the alpha veins being vestiges of the grain structure which existed in the gamma condition. On the other hand Northcott[1065] did not agree that passage through the gamma-alpha transformation is essential and supported the impurities theory. He found that veining was removed by annealing in hydrogen and was produced by annealing in contact with ferric oxide.

In addition to alpha veining Rawdon and Berglund[738] noted networks on etched ferrite grains which appeared to be associated with gamma and delta iron. The gamma and delta networks

did not appear simultaneously in the same specimen but either was often accompanied by alpha veining. The delta network (Fig. 9) was found only in ferrite in the cast or slightly worked condition and appeared as a relatively coarse network superimposed upon, but apparently unrelated to, the normal ferrite grain-boundary pattern. It consisted of minute inclusions in the ferrite which apparently outlined the grain structure of the iron when in the delta state. The delta network seemed
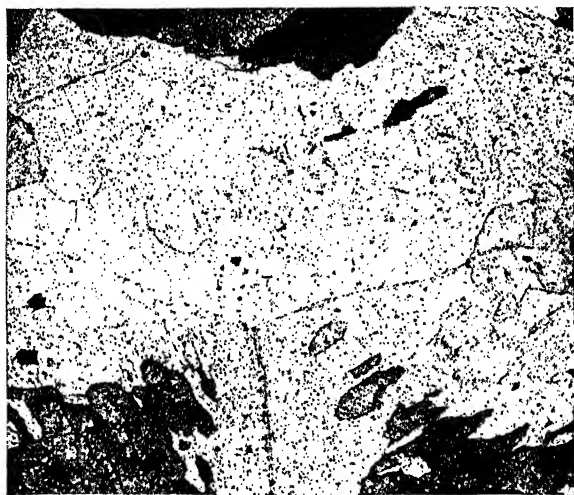
Fig. 9.—Delta network in ferrite grains. Etched with a saturated aqueous solution of ammonium persulphate. 50 ×. (*Rawdon and Berglund.*[738])

to be related to the hot shortness found in ferrite but otherwise was without effect upon the mechanical properties. The gamma network (Fig. 10) appeared superimposed upon the alpha grain boundaries but was found only in metal worked in the gamma condition or heated for a considerable length of time in the gamma temperature range. Like the delta network, its formation seemed to depend upon the presence of minute inclusions, possibly also upon a slight solid solubility of certain substances. It had little or no effect upon the mechanical properties of the iron.

59. Other Structures Found in Alpha Iron.—In a specimen of open-hearth iron which had been annealed in hydrogen for

100 hr. at 750 to 800°C., Rawdon and Berglund found evidence of twinning (Fig. 11), usually associated only with gamma iron. Mathewson[1018] stated that from theoretical considerations twinning would be expected to occur only exceptionally in pure iron, usually in the form of twin lamellae commonly called Neumann bands (Fig. 12); that the presence of impurities might stiffen the lattice sufficiently to permit twinning under favorable
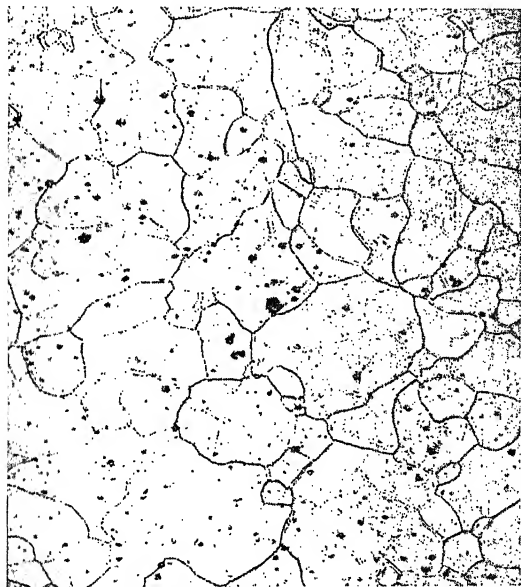
Fig. 10.—Gamma network in ferrite grains. Etched with 5 per cent alcoholic picric acid. 100×. (*Rawdon and Berglund.*[738])

circumstances; and that coarse-grained open-hearth ingot iron twins readily when deformed by impact.

It should be noted that the previously discussed networks, occurring throughout the entire crystal, are entirely different phenomena from the patterns produced by the various types of high-temperature or heat etching. Such patterns are surface markings only, outlining the structure of the metal at the particular temperature at which the etching treatment was applied. Most of the work on the structure of iron and steel as revealed
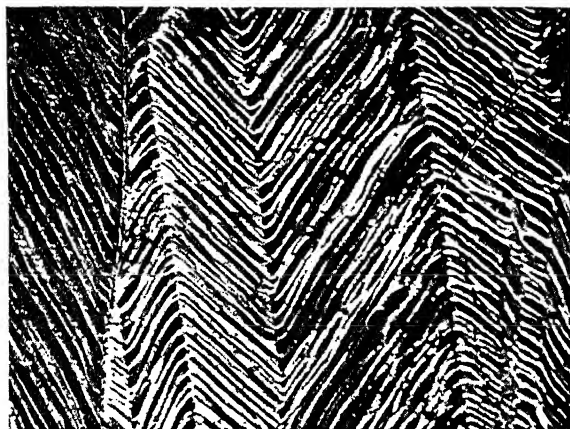
Fig. 11.—Twinning in open-hearth iron, heated for about 100 hr. in hydrogen at 750 to 800°C. 500×. (*Rawdon and Berglund.*[738])

Fig. 12.—Neumann bands in open-hearth iron. Etched with 5 per cent alcoholic picric acid. 250×. (*Rawdon and Berglund.*[738])

by heat-etching methods has been concerned with impure materials. Rawdon and Scott,[409] however, investigated the structure of electrolytic iron at 700, 880, and 950°C., the polished specimens being heated in an evacuated furnace for 30 min. at the selected temperatures. The volatilization of metal at the grain boundaries caused the formation of slight crevices which recorded the microstructure of the metal at the etching temperature. When the etching temperature was above the transformation temperature there was in addition a slight "buckling" of the surface, due to the volume change which accompanied the transformation. The buckling further accentuated the outline of the grain boundaries. Specimens heated to 700 and 880°C. showed a single network similar to that shown by iron etched at room temperature. The specimen heated to 950°C. showed two distinct patterns, one superimposed upon the other. One was similar in appearance to the usual ferrite structure, the other contained numerous straight lines and many inclosed grains having the appearance of twinned crystals.

An apparatus for the visual observation of the A_3 transformation was developed by Rogers.[855] A small specimen of polished iron was heated in a neutral atmosphere and the changes in appearance at different temperatures were noted. A phenomenon similar to the buckling described by Rawdon and Scott was observed at the A_3 transformation. The change did not occur instantaneously over the entire surface of the specimen but, on the contrary, originated at one side or in one corner and then spread over the surface. It was possible to record the successive stages of the transformation, as shown in Fig. 13, by means of a motion picture camera. Figure 14 is a picture of the transformation of alpha to gamma iron, taken at somewhat greater magnification than was used in Fig. 13.

By quenching basic open-hearth ingot iron from a temperature of about 1400°C., Tritton[743] obtained an acicular structure which he described as either the martensitic or Widmanstätten type. Quenching from 1000°C. gave only the normal ferrite structure. High-purity electrolytic iron did not have this martensitic structure after quenching from 1400°C. but electrolytic iron containing 0.05 per cent of carbon did. This suggested to Tritton that the presence of a small amount of carbon is
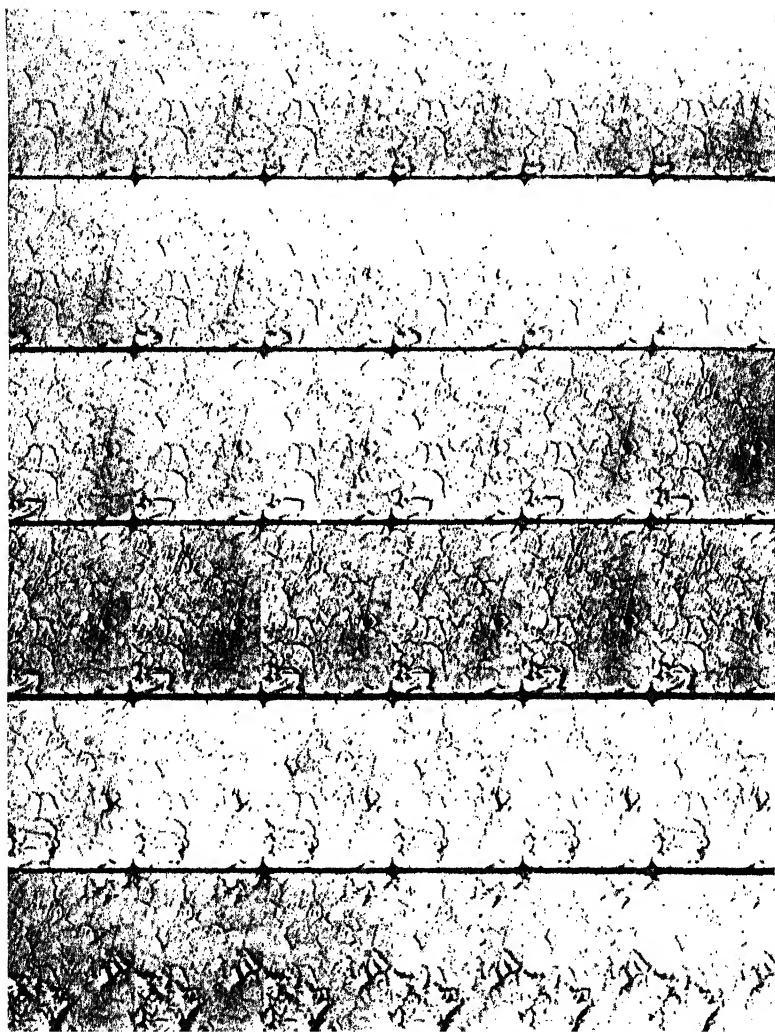
Fig. 13.—A_3 transformation sweeping over Armco iron. Heat etched. 30 ×.
(*Courtesy of B. A. Rogers.*)

responsible for the "martensitic" structure in quenched ingot iron. The hardness of the iron with this type of structure was very little greater than that of the same iron in the annealed condition.
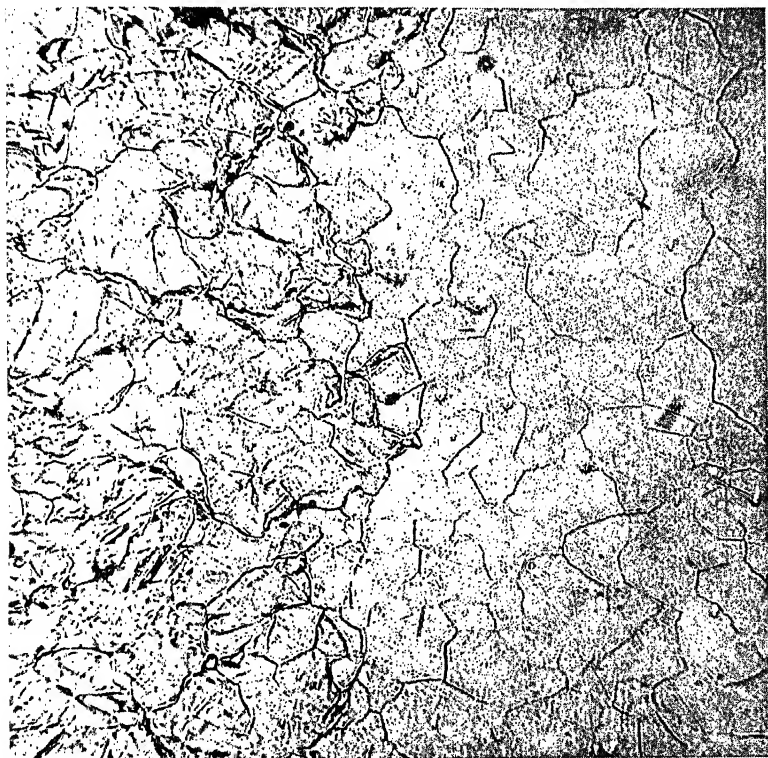
FIG. 14.—Transformation of alpha to gamma iron. Heat etched. 100×.
(*Rogers*.[855])

In a study of the orientation relationships between the gamma and alpha phases in iron of high purity, Mehl and Smith[1064] obtained Widmanstätten figures which resembled martensite in appearance. The material was electrolytic iron which had been purified by heating in a stream of undried hydrogen for 93 hr. at 1200°C. The carbon content of this iron was 0.004 per

cent. Very rapid quenching from temperatures between 950 and 1100°C. was necessary, but the optimum conditions for the development of the Widmanstätten figures could not be defined. Mehl and Smith stated that success in the development of the Widmanstätten figures was sporadic and unpredictable. The figures which were obtained delineated the (1 1 1) or octahedral planes of gamma iron.

D. AUTHORS' SUMMARY

There are three allotropic forms of high-purity iron, the alpha form stable at ordinary temperatures, the gamma form stable at intermediate temperatures, and the delta form stable at temperatures which approach the melting point. All three crystallize in the cubic system, alpha and delta iron as body-centered cubes, gamma iron as face-centered cubes. The lattice constant of alpha iron is 2.861 Å. at 20°C., that of gamma iron is 3.64 Å. at the temperature of the alpha-gamma transformation, and that of delta iron is about 2.92 Å. at the temperature of the gamma-delta transformation. The lattice constant of each of the three allotropic forms increases with increasing temperature in the range of existence of that form.

The allotropic transformations of alpha to gamma iron and of gamma to delta iron are known, respectively, as the A_3 and A_4 transformations. Earlier investigations indicated that an appreciable difference existed between the temperatures at which the A_3 transformation occurred on heating and on cooling, but recent work has shown that this difference can be reduced to only 1 or 2°C. through the use of purified specimens and very slow rates of heating and cooling. Hysteresis has not been observed in the A_4 transformation. It is suggested that 910°C. (1670°F.) and 1400°C. (2550°F.) be accepted, respectively, as the best present approximations for the temperatures of the A_3 and A_4 transformations.

In addition to the two allotropic transformations, iron undergoes a magnetic transition, the A_2 transition, from ferromagnetic to paramagnetic iron. The temperature at which the rate of change is most rapid, as determined by methods such as thermal analysis, is about 770°C. (1420°F.). The temperature at which the change is complete, as determined by magnetometric methods, is about 780°C. (1435°F.).

The existence of transformations other than the A_2 transition and the A_3 and A_4 transformations has not been established.

The microstructure of electrolytic iron varies with the conditions of deposition; such terms as fibrous, columnar, conical, nodular, and broken have been used to describe the appearance of different deposits of electrolytic iron. Crystalline grains, which are characteristic of the structure of pure metals in general, constitute the usual microstructure of high-purity iron, either of electrolytic or of other origin, after it has been melted. Various phantom structures and substructures, such as alpha veining and the formation of Widmanstätten figures, have been observed in certain grains of iron, but the significance of these figures and the conditions which are essential for their formation are still uncertain. Twinning is usually associated with gamma iron but has been observed in alpha iron as well. On theoretical grounds, twinning should be observed only rarely in very pure iron.

CHAPTER V

THERMAL PROPERTIES

*Melting Point, Vapor Pressure, and Boiling Point — Heat Capacity—
Thermal Conductivity — Thermal Expansivity — Authors' Summary*

The thermal properties of a metal are important to the producer of the raw material as well as to the user of the finished product. Melting operations and refining in the molten state must be carried out at temperatures above the melting point of the metal. The amount of heat required to reach such temperatures varies with the heat capacity of the metal. The upper limit to which a molten metal may be heated is its boiling point, but in the case of iron this property is of theoretical interest rather than of practical importance. The boiling point of iron is far above the melting point and also above the temperatures employed in melting and refining operations. Determinations of the vapor pressure of iron have been used chiefly to estimate the boiling point of the metal. At the temperatures to which iron is ordinarily subjected the tendency of the metal to vaporize is negligible. The heat capacity and thermal conductivity obviously are important in many uses of solid iron. The thermal expansion, that is, the change in dimensions with changing temperature, is of vital importance in iron or any other structural material.

A. MELTING POINT, VAPOR PRESSURE, AND BOILING POINT

Previous to 1904 the melting points ascribed to iron ranged from 1500 to 1804°C. The 1905 edition of Landolt and Börnstein's Tables reported the melting point of iron as between 1500 and 1600°C., an indication of the indefiniteness of the information available at that time. The early work on the melting point of iron was briefly reviewed by Carpenter.[174]

With the development of more precise high-temperature technique the subsequent history of the melting point of iron became largely a record of increasingly accurate values, due to

increasing purity in the materials used, to more effective precautions against contamination during the melting operation, and to adoption of a more accurate value for the constant C_2 in Wien's radiation formula, which is of fundamental importance in the calibration of the optical pyrometer.

60. Early Determinations of the Melting Point of Iron.— Carpenter and Keeling[121] in 1904 obtained the value 1505°C. for the melting point of a Swedish charcoal iron containing 0.11 per cent of recognized impurities. The iron was melted in magnesia in an atmosphere of carbon monoxide. The temperature scale was based on a platinum point of 1710°C. Correction to more recent values for the platinum point would raise the result of Carpenter and Keeling considerably. Burgess[153] determined the melting point of an electrolytic iron which contained 0.101 per cent of reported impurities, and that of a sample of Kahlbaum reduced iron; the former melted at 1507°C., the latter at 1499°C., both determinations being made by means of the micropyrometer. Harkort[157] reported 1504°C. as the melting point of a Swedish charcoal iron when melted in magnesia under carbon monoxide. Saklatwalla[184] obtained the value 1510°C. by melting electrolytic iron made by Merck's process in an Arsem furnace, using a magnesia crucible and a nitrogen atmosphere; the analysis of the iron was not given. Müller[196] found a rather impure electrolytic iron (reported impurities totaled 0.196 per cent) to have a melting interval of 1485 to 1525°C. and a freezing interval of 1505 to 1485°C. A freezing point of 1525°C. was found by Loebe and Becker[261] for a Swedish charcoal iron with 0.16 per cent of determined impurities; the iron was melted in porcelain under carbon monoxide.

During the years 1910 to 1917, Ruer and his coworkers made several determinations of the melting point of iron in connection with their study of iron-alloy systems. Ruer and Schüz[221] found that the freezing point of an ingot iron with 0.20 per cent of total reported impurities was 1502°C. Later, Ruer and Kaneko[292] and also Ruer and Fick[291] gave the melting point of the same material as 1524°C.

The investigations so far reviewed have been included as matters of interest but the results are of doubtful value in view of the lack of precision in methods and of the questionable purity of materials. The following investigations are con-

sidered by the authors to represent the best and most reliable work to date and the results of these investigations have been used in arriving at a probable value for the melting point of iron.

61. Later Determinations of the Melting Point. Ruer and Klesper[293] reported the freezing point of Langbein-Pfanhauser electrolytic iron as 1528°C. The impurities present in the material were reported to be: carbon 0.009 per cent; sulphur 0.001 to 0.002 per cent; copper 0.03 per cent; silicon, manganese, phosphorus, nickel, and chromium, none; total of determined impurities, 0.04 per cent. The iron was melted in porcelain in a nitrogen atmosphere. Temperatures were measured by thermocouples, with the upper temperature scale based upon 1451°C. as the melting point of nickel. If a correction is made to 1455°C., the nickel point[911,4] on the International temperature scale, the melting point of the iron becomes 1533°C. Rümelin and Fick[313] reported 1526°C. as the melting point of the same electrolytic iron but used Ruer and Klesper's value of 1528°C. in their tables. Ruer and Goerens[354] also reported 1528°C. as the melting point of this electrolytic iron. As the value 1528°C., reported several times by Ruer and his coworkers, was obtained on identical material and under the same conditions in each case, the value corrected to 1533°C. has been used but once in the derivation of an average value.

With the aid of an improved design of micropyrometer, Burgess and Waltenberg[300] determined the melting points of five different samples of high-purity iron. Three were electrolytic irons from different sources, one was Kahlbaum reduced iron in powder form, and one was iron reduced by hydrogen from Kahlbaum iron oxide. The compositions of these samples and the results obtained for their melting points are shown in Table 10. The derived value of 1533°C. was based upon the value 1549°C. for the palladium point. If a correction is made to 1555°C.—the palladium point[826,4] on the present scale—Burgess and Waltenberg's value for iron becomes 1538°C.

Melting point determinations were also made by Burgess and Waltenberg on crucible melts of electrolytic iron in vacuum and in hydrogen using an Arsem furnace. Temperatures were determined by an optical pyrometer. The average of six determinations, four in vacuum and two in hydrogen, was 1528°C., using a temperature scale based upon the value 1.450 cm.

TABLE 10.—MELTING POINT OF HIGH-PURITY IRON*

| Sample | Source | Composition, per cent | | | | | | | Melting point, °C. |
		C	Si	Mn	S	P	Cu	Total of determined impurities	
Electrolytic iron......	C. F. Burgess	0.012	0.013	0.00	0.00	0.004	.....	0.029	1534
Electrolytic iron......	Langbein-Pfanhauser	0.00	0.00	0.00	0.00	0.007	0.008	0.015	1532
Electrolytic iron......	J. R. Cain	0.004	0.001	0.00	0.004	0.0006	0.008	0.0176	1533
Iron powder..........	Kahlbaum	.....	.....	...	.....	......	.....	......	1534
Iron................	Kahlbaum's iron oxide reduced with hydrogen	.....	.....	...	.....	......	.....	......	1532
									Av. 1533 ± 1

* Burgess and Waltenberg.[300]

degrees for the constant C_2 in Wien's radiation formula. Correcting to 1.432 cm. degrees, the value on the present scale, Burgess and Waltenberg's value by the crucible method becomes 1536°C.

62. Recent Determinations of the Melting Point.—Hanson and Freeman[512] determined the melting point of a basic open-hearth ingot iron containing 0.012 per cent carbon, 0.017 per cent silicon, 0.07 per cent manganese, 0.017 per cent sulphur, and 0.014 per cent phosphorus. The total impurities determined were 0.130 per cent. Other impurities, particularly copper, nickel, cobalt, and oxygen, would be expected to be present but were not determined. This material, in fused alumina in a nitrogen atmosphere, melted at 1530°C. This temperature, measured with a thermocouple, was based upon the value 1452°C. for the nickel point. Corrected to the present value for the nickel point, 1455°C., the melting point of this iron becomes 1533°C.

Tritton and Hanson[585] obtained 1535°C. for the melting point of a sample of electrolytic iron which was reported to be free from silicon, sulphur, phosphorus, and manganese. Carbon was reported as a trace; the oxygen content was 0.277 per cent. Porcelain crucibles were used and the same melting-point value was obtained with either a nitrogen or an argon atmosphere. The temperature scale was based upon a palladium point of 1555°C., the accepted value at the present time.

Sykes[687] determined the melting point of iron prepared by ignition and reduction of ferrous oxalate precipitated from ferrous sulphate solution. From 0.1 to 0.2 per cent of iron oxide (0.02 to 0.06 per cent of oxygen) and less than 0.005 per cent of carbon were the only impurities reported although, in view of results at the Physikalisch-Technische Reichsanstalt[152,186] and elsewhere, it appears that small amounts of manganese and possibly other metals may have been present. The iron was melted in an alundum boat in an atmosphere of hydrogen. The melting point obtained was 1532°C. Sykes stated that his optical pyrometer was checked against the melting point of pure nickel but did not give the value used for the nickel point. If the nickel was pure and if 1452°C. (the accepted value for the nickel point in 1926) was used, Sykes' result corrected to 1455°C. (the present value for the nickel point) would be 1535°C. In view of the uncertainty as to his temperature scale, Sykes' value of 1532°C. is used in the average without correction.

Andrew and Binnie[815] melted basic open-hearth ingot iron in alundum crucibles in an atmosphere of mixed hydrogen and nitrogen, obtained by cracking ammonia, and determined the melting point by means of a tungsten-molybdenum thermocouple which had been calibrated against a platinum, platinum–rhodium thermocouple. The melting point obtained was 1537°C.

The melting point of a very carefully prepared electrolytic iron was determined by Jenkins and Gayler.[892] The iron, previous to its use for the melting-point determination, was melted in vacuum to remove gases and then remelted several times under hydrogen until particles of oxide were detected only with difficulty under the microscope. Impurities in the iron prior to the melting-point determination were: 0.005 to 0.007 per cent carbon, trace to 0.009 per cent silicon, trace of manganese, 0 to 0.001 per cent sulphur, 0.002 per cent phosphorus, trace to 0.006 per cent copper. As a check on the amount of contamination caused by the meltings, one ingot was analyzed after the melting-point determination. The content of impurities after melting was: 0.01 per cent carbon, 0.03 per cent silicon, 0.014 per cent phosphorus, 0.05 per cent oxygen, traces of manganese and sulphur. The iron was melted in alundum crucibles with high-frequency induced heating. Four different methods were used for obtaining black-body conditions, one being

the bubble method of Rosenhain, the other methods depending upon different arrangements of crucible and sighting tube. The optical pyrometer was calibrated by means of the gold point (1063°C.) and the palladium point (1555 ± 2°C.). Intermediate points were obtained by comparison with thermocouples. In the determination of temperatures at approximately the melting point of iron either an absorption screen or a sector disk was used to decrease the intensity of radiation.

Observations of both the melting and freezing points of iron were made during heating and cooling operations. Eighteen results were obtained, varying from 1524 to 1530°C., from which Jenkins and Gayler concluded that the melting point of iron was 1527 ± 3°C.

63. Summary of Melting-point Data.—In attempting to summarize these results and to arrive at a probable value for the melting point of iron, each of the investigations was reviewed from two angles: the purity of the iron and the accuracy of the temperature measurements. On this basis the results of seven investigations were selected for final consideration, as follows:

Investigator	Reported value, °C.	Corrected value, °C.
Ruer and Klesper[293]	1528	1533
Burgess and Waltenberg (micropyrometer)[300]	1533	1538
Burgess and Waltenberg (crucible method)[300]	1528	1536
Hanson and Freeman[512]	1530	1533
Tritton and Hanson[585]	1535	1535
Sykes[687]	1532	1532
Andrew and Binnie[815]	1537	1537
Jenkins and Gayler[892]	1527	1527
Average....		1534°C. (2793°F.)
Rounded to.		1535°C. (2795°F.)

The difficulty in comparing or in weighting these results is illustrated by the fact that the results of Burgess and Waltenberg and of Jenkins and Gayler constitute the upper and lower extreme limits, although, in the authors' opinion, these two are the outstanding investigations of the group. The probable

value for the melting point of iron was obtained, therefore, by a numerical rather than a weighted average of the corrected results. It is suggested that the value 1535°C. (2795°F.) be accepted as a rounded value for the best present approximation of the melting point of iron.

64. Vapor Pressure and Boiling Point. The value 2450°C. reported by Greenwood[192,257] as the boiling point of iron at atmospheric pressure, and much quoted in the literature, was criticized by Ruff and Bormann[312] as undoubtedly low, owing to contamination of the iron by iron oxide produced by the reaction between the molten iron and the magnesia lining of the graphite crucible. Ruff and Bormann used zirconia crucibles in their determination and obtained the value 2450 ± 50°C. as the boiling point at 36 mm. pressure. Ruff[247] determined the maximum temperature of iron arc electrodes, obtaining the value 2220°C. at 10 mm. pressure while Hagenbach and Langbein[399] found the temperature of the iron anode of an arc to be 2320°C. at atmospheric pressure.

By means of the Sackur and Tetrode equations, Millar[625] calculated the vapor pressure-temperature relation of iron from the data of Ruff and Bormann. Millar's computations indicated that the boiling point of iron was 3235°C. at 760 mm. pressure. The vapor-pressure data of Jones, Langmuir, and Mackay[724] given in Table 11 were calculated from their data on the rates of evaporation from an iron filament heated to various temperatures

TABLE 11.—VAPOR PRESSURE OF IRON*

Temperature, °C.	Vapor pressure, mm. Hg	Temperature, °C.	Vapor pressure, mm. Hg
327	1.86×10^{-23}	1427	7.6×10^{-3}
427	7.58×10^{-19}	1527	3.0×10^{-2}
527	2.06×10^{-16}	1727	2.9×10^{-1}
627	9.52×10^{-13}	1927	1.8
727	1.32×10^{-10}	2127	7.5
827	7.11×10^{-9}	2327	26.2
927	1.94×10^{-7}	2527	82.5
1027	3.22×10^{-6}	2727	165
1127	3.47×10^{-5}	2927	345
1227	2.70×10^{-4}	3127	630
1327	1.60×10^{-3}	3202	760

* Jones, Langmuir, and Mackay.[724]

in vacuum. Extrapolation to atmospheric pressure gave 3202°C. as the boiling point of iron. Ralston[853] averaged the values of Millar and of Jones, Langmuir, and Mackay and selected 3218°C. as the boiling point of iron.

Kelley[1078] recently computed the vapor pressure of iron at various temperatures, basing his computations on the calculations of free energy which were made by Overstreet. Kelley's results indicate that the boiling point of iron is 2735°C., according to the following data:

Temperature, °C.	1564	1960	2004	2316	2464	2595	2735
Vapor pressure, mm. Hg.	0.076	0.76	7.6	76	190	380	760

65. Summary of Data on Vapor Pressure and Boiling Point.— In view of the fact that the most reliable values were indirectly determined from data secured under experimental difficulties and with possible inaccuracies, a rounded value of 3000°C. (5430°F.) is suggested as expressing the probable boiling point of iron as closely as the data warrant.

B. HEAT CAPACITY

A survey of the literature on the heat capacity of iron reveals a decided lack of concordance in results, particularly for specific-heat values at temperatures above 1000°C. Ralston[853] in 1929 commented: "The heat capacity of iron and its alloys has been the subject of very much experimentation and yet such great discrepancies exist between even the best work that the whole matter is rather disappointing." Three years later, Austin[955] made the statement: "It may seem surprising that the heat capacity of iron, one of the most fundamental properties of one of our most useful substances, is still a matter for discussion, yet a survey of the existing information shows that the number of possible choices for a value at a certain temperature is roughly equal to the number of investigations including that temperature." This uncertainty, as Austin pointed out, is a result of several factors. Iron exists in different forms at different temperature ranges, undergoing two polymorphic transformations, each of which is accompanied by an energy change, and a magnetic transition which is accompanied by an anomaly in the

specific-heat curve. The technique of heat-capacity determinations at high temperatures is difficult and has not been developed to the point where results of high accuracy can be obtained. The previous mechanical and thermal history of a particular specimen may influence its heat capacity. Impurities, in view of their great effect on the magnetic properties of iron, may be expected to affect appreciably the magnetic component of its heat capacity. With the presence of these obstacles to accuracy, disagreement in results is not surprising. Only by a combination of greatly increased accuracy in methods and increased purity in material may we expect to obtain reliable results.

There are available two excellent critical reviews of the data on the thermal properties of iron, one by Ralston,[853] which includes data published through part of 1927, and the review by Austin [955,956] which appeared late in 1932. The values selected by Ralston were obtained by averaging the values for heat content reported by five investigators. From these average values the specific-heat values were derived. Austin's review included data obtained by improved methods and published subsequent to the summary by Ralston. Wherever it was possible, the values chosen by Austin were the ones which most nearly fulfilled theoretical requirements deduced from the thermodynamics of metal systems. Consequently Austin's selected values have been largely accepted in the present review. Throughout this text the rate of change in heat content at a particular temperature is termed the "specific heat," instead of the "true specific heat" as it is frequently expressed in the literature. The term "mean specific heat" is used to define the average rate of change in heat content over an appreciable temperature interval.

66. Heat Capacity of Alpha Iron at Low Temperatures.— The values for the specific heat of iron at low temperatures reported by Nordmeyer and Bernoulli[161] in 1907, by Nordmeyer[183] in 1908, and by Dewar[278] in 1913 were obtained by the method of mixtures over wide temperature intervals and are principally of historical interest. Determinations which are considered to be of merit begin with the work of Griffiths and Griffiths[281] who, in 1913, reported values for the specific heat of iron obtained by the more accurate method of electric heating whereby the rise in temperature, resulting from the addition

of a known amount of electric energy to a considerable mass of metal, was measured. The material used was basic open-hearth ingot iron having an iron content of 99.87 per cent by difference. Theoretical heat capacities were calculated by the formulae of Einstein, Nernst, and Lindemann and Debye. No one formula was capable of representing the experimental
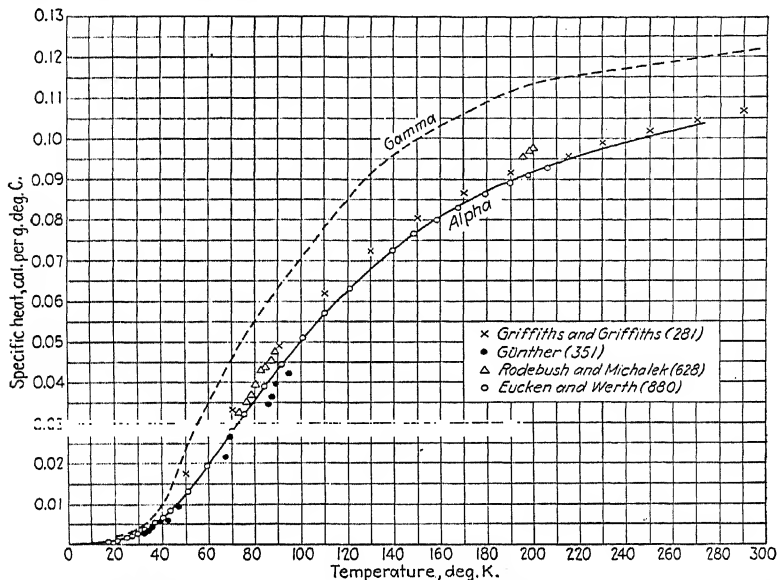
FIG. 15.—Specific heat of alpha iron at low temperatures. Both curves represent values selected by Austin.[955]

results over the entire temperature range. The formula of Debye gave the nearest approximation to the experimental values over the lowest portion of the range, but systematic divergencies occurred at the higher temperatures. The results of Griffiths and Griffiths, and of other selected investigations, are shown in Fig. 15.

Using the electric heating method of Nernst and Schwers, Günther[351] in 1916 determined the specific heat of iron in the temperature range 32 to 95°K. (−241 to −178°C.). Information as to the composition of the iron used was not included in Günther's paper.

On account of the serious discrepancies between the data of Griffiths and Griffiths and those of Günther, the results of the former being about a half a calorie per gram atom or 25 per cent higher than those of the latter at liquid air temperatures, Rodebush and Michalek[628] investigated the heat capacity of iron in the temperature range 72 to 200°K. (−201 to −73°C.). The determinations were made by the method of electric heating on a sample of high-grade commercial iron, stated to have an iron content of 99.88 per cent. The results, shown in Fig. 15, are in better accord with the results of Griffiths and Griffiths than with those of Günther.

Subsequent to the compilation by Ralston of his critical survey, Eucken and Werth[880] published their data on the heat capacity of electrolytic iron at low temperatures, obtained by the method of electric heating. Austin considered their results as the most complete and consistent of the available data. The selected values of Austin for alpha iron at low temperatures are given in Table 12 and are shown by a continuous line in Fig. 15. The dotted line in the figure shows the values selected by Austin for gamma iron at low temperatures, for comparison with the results for alpha iron.

TABLE 12.—SPECIFIC HEAT OF ALPHA IRON AT TEMPERATURES BELOW 0°C.*

Temperature		Specific heat	
°K.	°C.	cal. per g. °C.	cal. per g. atom °C.
20	−253	. . . . .	0.005
30	−243	0.003	0.105
40	−233	0.007	0.367
50	−223	0.013	0.710
75	−198	0.032	1.80
100	−173	0.051	2.85
125	−148	0.065	3.65
150	−123	0.077	4.33
175	− 98	0.086	4.80
200	− 73	0.092	5.15
225	− 48	0.097	5.40
250	− 23	0.101	5.66
273.1	0	0.104	5.84

* Austin.[955]

67. Heat Capacity of Gamma Iron at Low Temperatures.—
The gamma phase in high-purity iron is not stable below 900°C.,
consequently it is not possible to determine directly the heat
capacity of gamma iron at temperatures lower than this.   How-
ever, by the addition of a sufficient amount of an alloying
element such as nickel or manganese, which is more soluble in
gamma than in alpha iron, the transition temperature of gamma
to alpha iron can be lowered to a point where the velocity of
the transformation is practically zero.   From the heat capacities
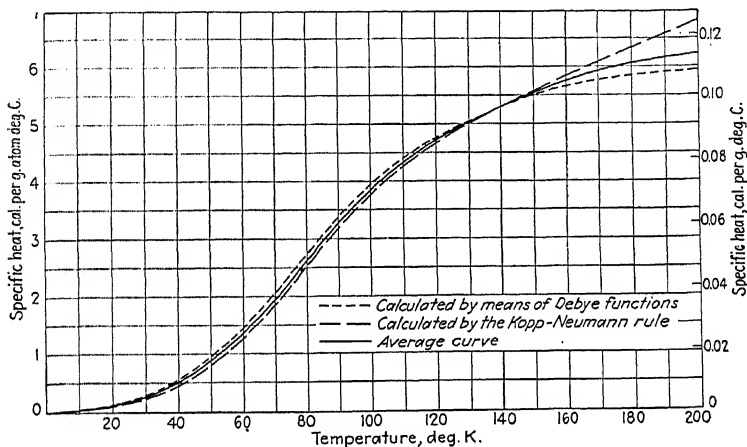
Fig. 16.—Specific heat of gamma iron at low temperatures.   (*Austin.*[955])

of a series of such alloys of known composition the heat capacity
of gamma iron can be calculated by extrapolation to zero con-
centration of the alloying element.

Eucken and Werth[880] determined the heat capacity at low
temperatures of iron-manganese alloys containing 50, 30, and
19.4 per cent of manganese.   From these data the specific heat
of gamma iron at the various temperatures was calculated by
two methods, by use of the Kopp-Neumann rule and by use of a
Debye frequency.   According to Eucken and Werth's curves,
the two methods did not give identical values.   Numerical
values for the specific heat of gamma iron, shown in Table 13
and Fig. 16, were calculated by Austin[955] from the data of
Eucken and Werth.

TABLE 13.— SPECIFIC HEAT OF GAMMA IRON AT TEMPERATURES BELOW 0°C.*

Temperature		Specific heat	
°K.	°C.	cal. per g. °C.	cal. per g. atom °C.
20	−253	. . . . .	0.10
30	−243	0.004	0.25
40	−233	0.010	0.53
50	−223	0.024	1.36
75	−198	0.052	2.90
100	−173	0.071	3.95
125	−148	0.089	5.00
150	−123	0.100	5.60
175	−98	0.109	6.10
200	−73	0.114	6.35
225	−48	0.116	6.50
250	−23	0.118	6.60
273.1	0	0.120	6.70
298	+25	0.122	6.80

* Austin.[955]

68. Heat Capacity of Alpha Iron at Temperatures above 0°C.—The early work on the heat capacity of iron at elevated temperatures was largely on impure iron by methods deficient in accuracy and can be dismissed as unimportant. The work previous to 1893 was reviewed by Richards.[60] The investigation by Harker[131] in 1905 deserves mention, more because his results for temperatures below 900°C. are in fair accord with recent values than because of any indication of unusual accuracy of his method in the published account of his work. The values reported by Oberhoffer[162] in 1907 were, in general, considerably higher than those of recent investigations although his apparatus, a modified Bunsen ice calorimeter, was superior to that of Harker. Oberhoffer's paper included a review of previous work and an excellent bibliography. The data reported in 1908 by Weiss and Beck,[187] while of doubtful accuracy as the iron was not protected from oxidation, are of interest as first bringing out the anomalous character of the specific-heat curve in the vicinity of the magnetic transformation. The specific heat was found to increase rapidly to a maximum as the A_2

temperature was approached and then to drop abruptly to a low value as the iron became paramagnetic. This finding was later confirmed by Weiss, Piccard, and Carrard[359] who used a calorimeter of improved design and two specimens of electrolytic iron, one of which was gold plated to prevent oxidation. Their results, with those of subsequent investigators, are shown in Fig. 17.
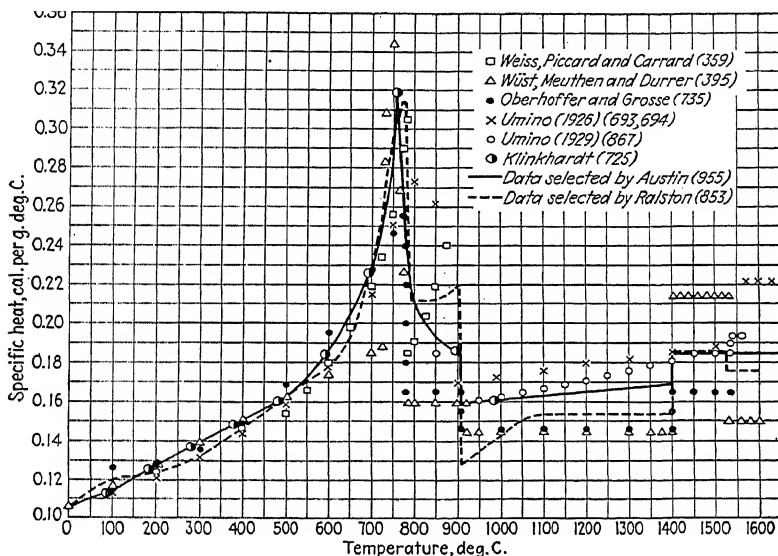
Fɪɢ. 17.—Specific heat of iron at elevated temperatures.

The specific-heat data reported by Wüst, Meuthen, and Durrer[395] were generally accepted as the most precise available for nearly a decade following their publication in 1918. The values given were for electrolytic iron and were determined in the Oberhoffer modification of the Bunsen ice calorimeter. The specific-heat curve of Wüst and his coworkers differed in the range of the magnetic transformation from that of Weiss, but Ralston[853] replotted the heat-content data of Wüst and derived the specific heats, obtaining a curve similar to that of Weiss. Wüst evidently smoothed his heat-content curve on the assumption that deviation from a smooth curve was due to experimental

errors.   Wüst, Meuthen, and Durrer carried their measurements
up to 1600°C., permitting determination of the heat effects of
the transformation points and of the heat of fusion.   Because of
the discrepancies in the A_2 range between the data of Wüst and
those of Weiss, Oberhoffer and Grosse[735] repeated the work,
using the ice calorimeter and electrolytic iron which contained
0.036 per cent of reported impurities.   Their results confirmed
those of Weiss with respect to the form of the specific-heat
curve.

The first investigation by Umino[693] was the determination
of the specific heats of a series of twelve carbon steels with carbon
contents from 0.09 to 2.84 per cent.   From extrapolation of these
data he obtained values for the specific heats of carbon-free
iron.   These values cannot, however, be accepted as representa-
tive of pure iron since the reported impurities, exclusive of
carbon, in Umino's steels ranged from 0.41 to 2.03 per cent.
Umino[694] also reported values for the specific heat between 100
and 1630°C. of an iron containing 0.30 per cent of reported
impurities; of an electrolytic iron for the temperature range 680
to 960°C.[745] and, in 1929,[867] for the range 680 to 1560°C.
Umino in all of his work used the method of mixtures with an
atmosphere of hydrogen to prevent oxidation.   His results are
included in Fig. 17.

In a study of the heat capacity of vacuum-melted electrolytic
iron Klinkhardt[725] made use of an aneroid calorimeter in which
the iron, in a high vacuum, was heated through small temperature
intervals by electron bombardment and the rise in temperature
caused by a measured energy input was measured by means of a
thermocouple.   In this way the specific heat was determined
directly over the temperature range 100 to 1000°C., as shown
in Fig. 17.   Klinkhardt also determined the specific heats of a
series of iron-manganese alloys in which the iron existed in the
gamma state.   By extrapolation to zero manganese content,
Klinkhardt obtained values for the specific heat of gamma iron
between 100°C. and the A_3 point, in addition to his directly
determined values for temperatures between the A_3 point and
1000°C.

Ralston[853] computed values for the specific heat of iron by
plotting the heat content versus temperature data of Weiss and
Beck,[187] Weiss, Piccard, and Carrard,[359] Wüst, Meuthen,

and Durrer,[395] Oberhoffer and Grosse,[735] and Umino[693,694,745] and then drawing an average curve from which the specific heats were derived. Yap[988] calculated the specific heats of iron, at temperatures between 0°C. and the A_3 point, but these calculations were based entirely on the data of Umino. Austin[955] selected the data of Griffiths and Griffiths[281] for the specific heat

TABLE 14.—SPECIFIC HEAT OF ALPHA IRON AT TEMPERATURES BETWEEN 0°C. AND THE A_3 POINT*

Temperature		Specific heat	
°K.	°C.	cal. per g. °C.	cal. per g. atom °C.
273.1	0	0.1045	5.835
283	10	0.1060	5.919
293	20	0.1075	6.002
298	25	0.1080	6.051
303	30	0.1087	6.070
313	40	0.1097	6.126
323	50	0.1105	6.170
333	60	0.1112	6.209
343	70	0.1119	6.248
353	80	0.1126	6.288
363	90	0.1133	6.322
373	100	0.1141	6.395
423	150	0.121	6.78
473	200	0.128	7.13
523	250	0.134	7.48
573	300	0.140	7.82
623	350	0.146	8.14
673	400	0.151	8.43
723	450	0.157	8.74
773	500	0.163	9.10
823	550	0.172	9.58
873	600	0.188	10.54
923	650	0.208	11.62
973	700	0.230	12.84
1023	750	0.276	15.40
1033	760	0.320	17.89
1073	800	0.210	11.70
1123	850	0.194	10.84
1173	900	0.186	10.39
1179	906	0.160	9.94

* Austin.[955]

of alpha iron between 0° and 100°C. and those of Klinkhardt[725] for temperatures between 100°C. and the A_3 point. The selected data of Austin are given in Table 14.

69. Heat Capacity of Gamma Iron.—The divergence of opinion regarding the heat capacities of iron at different temperatures is particularly noticeable in the range in which gamma iron is the stable form. Harker's data[131] indicated a decrease in the specific heat of gamma iron with increasing temperature, but his results are of doubtful value in view of the state of calorimetry and pyrometry at that time (1905). Wüst, Meuthen, and Durrer[395] and Oberhoffer and Grosse[735] concluded that the specific heat of gamma iron did not vary with temperature. Umino[694,867] and Klinkhardt[725] found that it increased with increasing temperature. Ralston's review[853] of the heat-content data of a number of investigators indicated that it increased between the A_3 point and 1100°C. but remained constant at temperatures above 1100°C. Yap[988] computed the specific heat of gamma iron from the data of Umino. Aus-

TABLE 15.— SPECIFIC HEAT OF GAMMA IRON AT TEMPERATURES BETWEEN 0° AND 1500°C.*

Temperature, °C.	Specific heat		Temperature, °C.	Specific heat	
	cal. per g. °C.	cal. per g. atom °C.		cal. per g. °C.	cal. per g. atom °C.
0	0.120	6.70	800	0.158	8.88
50	0.124	6.90	850	0.159	8.91
100	0.127	7.11	900	0.160	8.98
150	0.131	7.30	950	0.161	8.99
200	0.134	7.49	1000	0.162	9.02
250	0.137	7.67	1050	0.162	9.05
300	0.141	7.86	1100	0.163	9.10
350	0.143	8.01	1150	0.164	9.16
400	0.146	8.18	1200	0.165	9.21
450	0.148	8.30	1250	0.166	9.27
500	0.151	8.43	1300	0.167	9.32
550	0.153	8.54	1350	0.168	9.38
600	0.155	8.66	1400	0.169	9.44
650	0.156	8.71	1450	0.170	9.50
700	0.157	8.77	1500	0.171	9.56
750	0.158	8.81			

* Austin.[988]

tin[955] averaged the values of several investigators,[395,725,735,867] weighting Umino's values[867] at three times the others, and considered it probable that the specific heat of gamma iron increases with increasing temperature between the A_3 and A_4 points. The selected values of Austin[955] between 0° and 1500°C. are given in Table 15. Austin accepted Klinkhardt's[725] values for temperatures between 0°C. and the A_3 point; the values for temperatures above 1400°C. were obtained by extrapolation.

70. Heat Capacity of Delta Iron and Liquid Iron.—Of the four sets of data available on the specific heat of delta iron, three indicate that it is constant throughout the temperature range. Umino's 1926 values[694] showed an increase between 1400 and 1500°C. The reported values of these four investigations are:

Investigator	Tempera-ture, °C.	Specific heat	
		cal. per g. °C.	cal. per g. atom °C.
Wüst, Meuthen, and Durrer[395]	1420	0.2142	11.97
Umino[694]	1500	0.187	10.45
Oberhoffer and Grosse[735]	1401 to 1528	0.165	9.22
Umino[867]	1500	0.185	10.33

Ralston[853] derived the value 0.143 cal. per g. °C. from his heat content versus temperature curve. This value was lower than that for gamma iron, which Austin stated[955] is incompatible with thermodynamic requirements. If Ralston's heat-content data are plotted against temperature, there is evidence of error in the value given at 1535°C.; between 1400 and 1500°C. the heat content versus temperature relation is a straight line with a slope of 0.189 cal. per g. °C. which is about an average of the values of the investigators whose data Ralston used; between 1500 and 1535°C. the line has a slope of 0.060 cal. per g. °C., an improbable value. Extrapolation of the data between 1400 and 1500°C. gives 256.7 cal. per g. for the heat content at 1535°C., but Ralston used 252.3 in obtaining his value of 0.143 cal. per g. °C. for the specific heat of delta iron. The specific-heat value derived from the major portion of Ralston's heat content versus temperature curve, 0.189 cal. per g. °C., is in good agreement

with Umino's value 0.185 cal. per g. °C., which Austin has selected as the most probable. Yap[988] also accepted Umino's value for delta iron.
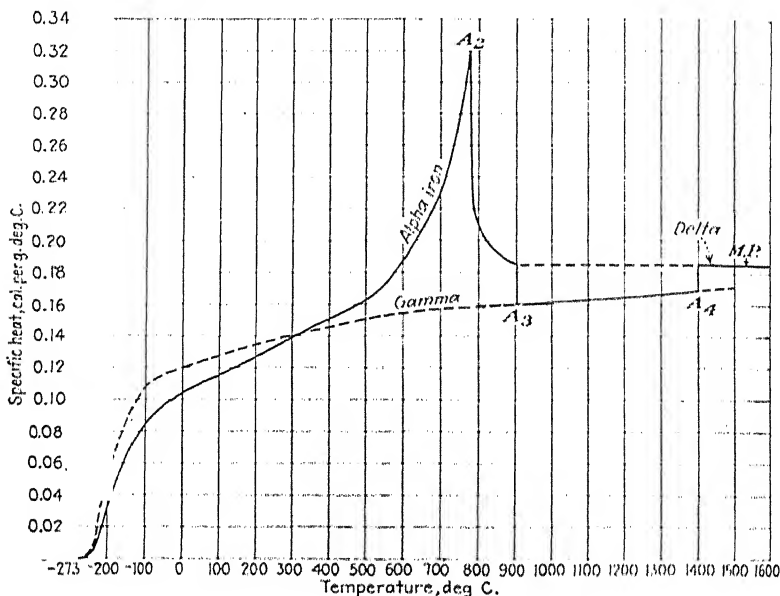
FIG. 18.   Specific heat of iron.   (*Austin.*[966])

The four determinations available for the specific heat of liquid iron are as follows:

Investigator	Temperature, °C.	Specific heat, cal. per g. °C.
Wüst, Meuthen, and Durrer[395]	1528 to 1600	0.150
Umino[694]	1570 to 1600	0.222
Oberhoffer and Grosse[735]	1528 to 1590	0.142
Umino[867]	1540 to 1560	0.194

From the first three Ralston derived the value 0.174 cal. per g. °C. Austin averaged the values, giving the first three a weight of

one, the last a weight of three, and derived the value 0.185 cal. per g. °C. as a probable value for the specific heat of liquid iron.

Austin's summary[955] of available information for the heat capacity of iron, at all temperatures at which observations have been made, is shown in Fig. 18.

71. Heat Effect at the A_2 Point.—Values ranging from 1.0 to 6.56 cal. per g. have been reported as the heat effect at the
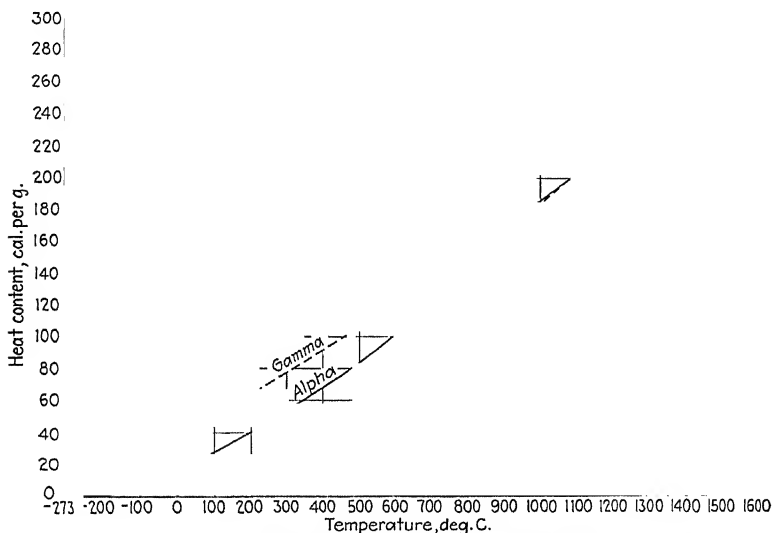
Fig. 19.—Heat content of iron. (*Austin.*[956])

A_2 point, but the data do not show any discontinuity in the heat content (Fig. 19) or even in specific heat at this point. Hence, there is probably no heat of transition at the A_2 point. With increasing temperature, the heat content rises at an increasing rate as the A_2 point is approached and at a decreasing rate after this point is passed. The values which have been reported as heats of transition should be considered differences in heat content over temperature intervals.

72. Heat Effect at the A_3 Point.—The values which have been reported for the heat of transition at the A_3 point are given in Table 16.

TABLE 16.— HEAT OF TRANSITION AT THE A_3 POINT

Investigator	cal. per g.	cal. per g. atom
Osmond[36]	3.8	216
Stansfield[91]	2.86	160
Meuthen[262]	5 to 6	279 to 335
Wüst, Meuthen, and Durrer[395]	6.56	366
Umino[694]	5.35	299
Oberhoffer and Grosse[735]	6.76	375
Klinkhardt[725]	3.86*	216
Umino[867]	5.60	313
Esser and Bunghardt[1053]	}3.6* }3.42*	}201 }191

* Determined directly.

With the exception of the values of Klinkhardt[725] and of Esser and Bunghardt,[1053] these values were determined as the difference in heat content below and above the transformation point. They are then the small differences between two large values, neither of which has been determined precisely, which accounts for the discrepancies found in the reported values. Ralston[853] obtained 4.9 cal. per g. from an average heat-content curve. Since Ralston compiled his review, Klinkhardt measured directly the heat absorbed in the transformation and obtained 3.86 cal. per g. or 216 cal. per g. atom, which value Austin[955] selected as the most probable for the heat of transition at the A_3 point. The direct determinations which were made subsequently by Esser and Bunghardt substantially confirm the results obtained by Klinkhardt.

Yap[988] computed the heat effect which accompanies the occurrence of the alpha-gamma transformation at temperatures other than that of the A_3 point. These computations were based on Umino's heat-content data. According to Yap's computations, the heat effect increases with decreasing temperature below the A_3 point, from 5.6 cal. per g. at 900°C. to 8.5 at 800°C., 18.4 at 600°C., and 22.6 and 22.4 cal. per g., respectively, at 400 and 200°C. At temperatures above the A_3 point, the heat effect decreases with increasing temperature from 3.2 cal. per g. at 1000°C. to 1.2 at 1100°C., −0.3 at 1200°C., −1.5 at 1300°C., and −1.9 cal. per g. at 1400°C. The minus sign at temperatures of 1200°C. and higher signifies that the transition

becomes exothermic at some temperature between 1100 and 1200°C.

73. Heat Effect at the A_4 Point.—The heat effect at the A_4 point was variously reported to be 1.94 cal. per g.,[395] 3.00 cal. per g.,[694] and 2.53 cal. per g.[735] Ralston[853] plotted a heat-content curve from an average of the best data available and obtained 1.7 cal. per g., or 95 cal. per g. atom, as the heat of transition at the A_4 point. This value was appreciably lower than those previously reported, due, in Ralston's opinion, to the practice of the earlier investigators of "smoothing" their heat content versus temperature curves. Subsequently, Umino[867] reported 1.86 cal. per g., in fair agreement with Ralston's value. Austin[955] considered Ralston's value as the most probable one for the heat effect at the A_4 point.

74. Heat of Fusion.—The early values for the heat of fusion of iron were derived from indirect computations rather than by direct determinations. It is of interest that some of these early values are in better agreement with the best of the recent values than are some obtained by direct determination.

Person[6] in 1848 made use of an equation which compared the heat of fusion, modulus of elasticity, and density of one metal with the same properties of a second metal. With zinc as the reference metal a value of 60 cal. per g. was obtained for the heat of fusion of iron. By a similar method, Guldberg[115] obtained the value 64 cal. per g.   Richards[76] used an equation derived from Pictet's rule and predicted the heat of fusion to be about 69 cal. per g. Brisker's calculation[173] was based on the van't Hoff equation for depression of the freezing point by solutes.   Using 1500 and 1130°C., respectively, as the melting points of pure iron and of iron containing 4.3 per cent of carbon, he obtained 31.646 cal. per g. as the heat of fusion. Brisker assumed the molecules of dissolved carbon to be diatomic, probably because this gave a value in agreement with observed values for cast iron.   Ralston recalculated the heat of fusion by Brisker's method, using 12 as the molecular weight of carbon and 1535°C. as the melting point of iron, and obtained 57.5 cal. per g. as the heat of fusion.   However, he demonstrated by data on other metals that the method of Brisker is not reliable.

The first calorimetric determination of the heat of fusion of high-purity iron was that of Wüst, Meuthen, and Durrer[395] in

1918. Using electrolytic iron in a vacuum calorimeter, they obtained the value 49.35 cal. per g. Oberhoffer and Grosse[735] used the same method and reported 64.38 cal. per g. The first value reported by Umino,[694] 69.20 cal. per g., was obtained on steel. Later, Umino[867] determined the heat of fusion of electrolytic iron as 65.65 cal. per g. The method of mixtures was used with a hydrogen atmosphere to prevent oxidation.

Yap[953] calculated the heat of fusion of pure iron from data on the depression of the freezing point, with a correction for the heat of dissociation of iron carbide. His value was 64.4 cal. per g. Pobořil[1067] obtained 64.2 cal. per g. for the heat of fusion of pure iron by calculation from the data of Wever and Jellinghaus on iron-vanadium alloys.

The values which have been reported by various observers for the heat of fusion are given in Table 17.

TABLE 17.— HEAT OF FUSION OF IRON

Investigator	Method	cal. per g.	cal. per g. atom
Person[6]	Calculation	60	3353
Richards[76]	Calculation	69	3854
Guldberg[115]	Calculation	64	3575
Brisker (corrected)[173]	Calculation	57.5	3212
Wüst, Meuthen, and Durrer[395]	Ice calorimeter	49.35	2757
Umino[694]	Method of mixtures	69.2	3864
Oberhoffer and Grosse[735]	Ice calorimeter	64.36	3595
Umino[867]	Method of mixtures	65.65	3664
Yap[953]	Calculation	64.4	3596
Pobořil[1067]	Calculation	64.2	3585

Ralston[853] selected 64.9 cal. per g., which value Austin[955] accepted as the best available. Inasmuch as the reported data indicate that even the unit figure is in doubt, the authors suggest that the rounded value of 65 cal. per g. (3630 cal. per g. atom) be accepted as the best present approximation for the heat of fusion of iron.

75. Entropy, Heat Content, and Free Energy.—Three groups of data are available for the entropy of iron: those of Ralston,[853] of Yap,[988] and of Austin.[955] The entropy values reported by Ralston were computed from specific-heat values obtained from

data of several investigations as previously mentioned. Yap's values were based on Umino's data. Austin's entropy values were obtained largely from directly determined specific-heat values, his heat-content data (Fig. 19) being also derived from the specific-heat data. Due to the erroneous values used by Ralston for the heat content of iron at 1535°C. and for the specific heat of delta iron, his data for the heat content of iron at temperatures of 1535°C. and higher and his values for the entropy of iron above 1400°C. were in error. After correction of Ralston's data, the three sets of data are in close agreement.

From thermodynamic consideration of thermal data, Kelley[1078] calculated that the heat of vaporization of iron at the boiling point (which he considered to be 2735°C.) is 1515 cal. per g. or 84,620 cal. per g. atom. He also derived formulas for the calculation of the heat of vaporization of iron at other temperatures.

Austin's data for the entropy, heat content, and free energy of alpha and delta iron are given in Table 18 and for gamma iron in Table 19.

Two sets of data were given by Austin for the heat content of gamma iron, one based on zero at 0°K. (-273°C.), the second based on 960 cal. per g. atom at 0°K. The latter value makes the heat content of gamma iron at 906°C. greater than that of alpha iron by 218 cal. per g. atom, the heat of transformation at that temperature, thus permitting comparison of the heat contents of the two modifications. A typographical error which occurred in Austin's paper, 11.44 instead of 12.44 being given for the entropy of gamma iron at 250°C., has been corrected in reproducing his data. Austin pointed out that his data (Tables 18 and 19) are not entirely consistent from a thermodynamic standpoint, in that the free energies of alpha and gamma iron should be equal at the A_3 transformation and again at the A_4 transformation. However, Austin considered that the discrepancies were within the range of experimental error and for practical purposes insignificant.

Kelley[1078] recently calculated the free energy of vaporization of iron from 0°C. to temperatures above the melting point.

76. Summary of Heat Capacity of Iron.—The form of the specific heat versus temperature curve of iron below the A_2 point is definitely established although there is some disagreement among the various investigators as to the numerical values.

TABLE 18.—HEAT CONTENT, ENTROPY, AND FREE ENERGY OF ALPHA IRON*

Temperature		Entropy (S), cal. per g. atom °C.	Heat content (H), referred to $H = 0$ at 0°K.		Free energy (F), $F = H - TS$, cal. per g. atom
°K.	°C.		cal. per g.	cal. per g. atom	
0	−273.1	0.0	0.0	0	0
50	−223.1	0.248	0.09	5	− 8
100	−173.1	1.40	1.88	105	− 45
150	−123.1	2.83	5.20	290	− 134
200	− 73.1	4.24	9.4	525	− 303
250	− 23.1	5.53	14.5	810	− 572
273.1	0	6.10	17.0	950	− 715
298	25	6.60	19.6	1096	− 871
323	50	7.01	22.4	1250	− 1014
373	100	8.10	28.0	1566	− 1455
423	150	8.94	33.9	1894	− 1887
473	200	9.80	40.2	2246	− 2389
523	250	10.44	46.7	2610	− 2850
573	300	11.11	53.7	2998	− 3368
623	350	11.82	60.8	3394	− 3970
673	400	12.48	68.2	3814	− 4585
723	450	13.07	76.0	4244	− 5206
773	500	13.72	84.0	4689	− 5911
823	550	14.26	92.4	5159	− 6581
873	600	14.83	101.2	5653	− 7293
923	650	15.42	111.1	6204	− 8028
973	700	16.14	122.0	6810	− 8894
1023	750	16.53	133.4	7451	− 9460
1073	800	17.45	146.0	8151	−10573
1123	850	18.08	156.5	8737	−11566
1173	900	18.48	165.6	9250	−12427
1170	906	18.51	166.4	9294	−12500
1223	950	18.86	174.9	9765	−13300
1273	1000	19.27	184.1	10280	−14251
1323	1050	19.66	193.5	10795	−15215
1373	1100	20.05	202.5	11310	−16219
1423	1150	20.42	211.8	11825	−17233
1473	1200	20.76	221.0	12340	−18239
1523	1250	21.13	230.3	12855	−19325
1573	1300	21.43	239.4	13370	−20339
1623	1350	21.77	248.6	13885	−21448
1673	1400	22.08	257.9	14400	−22540
1723	1450	22.38	267.1	14915	−23645
1773	1500	22.68	276.3	15430	−24782
1808	1535	22.88	282.8	15791†	−25400

* Austin.[955]
† Corrected for 1535 instead of 1550°C.

TABLE 19.—HEAT CONTENT, ENTROPY, AND FREE ENERGY OF GAMMA IRON*

Temperature		Entropy (S), cal. per g. atom °C.	Heat content (H_1), based on $H_1 = 0$ at 0°K.		Heat content (H_2), based on $H_2 = 960$ at 0°K.		Free energy (F), $F = H_2 - TS$, cal. per g. atom
°K.	°C.		cal. per g.	cal. per g. atom	cal. per g.	cal. per g. atom	
0	−273.1	0.0	0.0	0.0	17.19	960	960
23	−250	0.06	0.018	1.0	17.21	961	957
73	−200	1.20	1.196	66.8	18.37	1026	939
123	−150	3.08	4.67	261	21.9	1221	842
173	−100	4.98	9.63	538	26.8	1498	636
223	− 50	6.66	15.4	862	32.6	1822	336
273	0	7.90	21.2	1185	38.4	2145	− 12
298	25	8.54	24.3	1357	41.5	2317	− 228
323	50	9.00	27.5	1529	44.6	2489	− 420
373	100	9.94	33.7	1880	50.5	2840	− 867
423	150	10.83	40.2	2244	57.6	3214	− 1377
473	200	11.65	46.9	2617	64.1	3577	− 1933
523	250	12.44†	53.65	2996	70.8	3956	− 2550
573	300	13.14	60.6	3384	77.8	4344	− 3185
623	350	13.80	67.7	3781	84.9	4741	− 3856
673	400	14.40	75.0	4186	92.2	5146	− 4545
723	450	15.00	82.4	4601	99.6	5561	− 5284
773	500	15.60	89.8	5016	107.0	5976	− 6083
823	550	16.05	97.5	5442	114.6	6402	− 6807
873	600	16.54	105.1	5872	122.4	6832	− 7607
923	650	17.03	112.9	6307	130.1	7267	− 8452
973	700	17.49	120.8	6744	136.2	7604	− 9314
1023	750	17.85	128.7	7184	145.8	8144	−10116
1073	800	18.33	136.5	7625	153.7	8585	−11083
1123	850	18.70	144.5	8069	161.7	9029	−11971
1173	900	19.13	152.5	8515	169.7	9475	−12954
1179	906	19.17	153.3	8552	170.3	9512	−13004
1223	950	19.50	160.5	8961	177.7	9921	−13524
1273	1000	19.86	168.5	9411	185.7	10371	−14911
1323	1050	20.21	176.6	9862	193.8	10822	−15916
1373	1100	20.55	184.8	10319	202.0	11279	−16940
1423	1150	20.87	192.9	10774	210.1	11734	−17964
1473	1200	21.19	201.2	11234	218.1	12194	−19020
1523	1250	21.52	209.4	11695	226.6	12655	−20120
1573	1300	21.80	217.8	12160	236.6	13120	−21171
1623	1350	22.09	226.1	12627	242.8	13587	−22265
1673	1400	22.37	234.6	13098	251.8	14058	−23367
1723	1450	22.65	243.0	13571	260.2	14531	−24495
1773	1500	22.92	251.6	14048	268.8	15008	−25630

* Austin.[966]
† Corrected, typographical error in original data.

As Austin pointed out, the accuracy of the most reliable data, those of Klinkhardt, is probably sufficient for practical purposes.

Above the A_2 point the situation is less satisfactory, the disagreement extending to the form of the curve as well as to the values. Some investigators, including Klinkhardt, have reported that the specific heat of iron decreases gradually from the A_2 to the A_3 point. Others have reported that it drops precipitously at the A_2 point to a minimum followed by a gradual increase to the A_3 point; and others reported a precipitous drop at the A_2 point to a value which remained constant to the A_3 point. Klinkhardt's values are preferred.

Between the A_3 and A_4 points the specific heat has been depicted as remaining constant throughout the range, as increasing over part of the range and then remaining constant, and as increasing gradually over the entire range. The specific heat of delta iron has been reported as increasing in value with temperature and as remaining constant. The specific heat of molten iron has been reported as higher than, lower than, and the same as that of delta iron at the melting point. Serious discrepancies are found in the values reported for the heat effects at the transformation points and at the melting point. The doubtful accuracy of the data for the specific heat at high temperatures naturally applies to the related data for heat content, free energy, and entropy. A survey of the existing data indicates the need for more precise determinations of the heat capacity of iron, particularly for gamma and delta iron.

The heat-capacity values selected by Austin, after consideration of both the thermodynamic requirements and the comparative accuracy of the methods used by the various investigators, seem the most probable representation now available for the heat capacity-temperature relationship of high-purity iron.

C. THERMAL CONDUCTIVITY

Investigations of the thermal conductivity of iron have been confined largely to impure material, and only a few data are available on high-purity iron.

The work previous to 1896 was briefly reviewed by Holborn and Wien.[70] The mean of the previously reported values was 0.156 cal. per sec. per sq. cm. (°C. per cm.) for thermal conductivity and 0.000167 for the temperature coefficient. In

1900 Hall[93] obtained 0.1528 cal. per sec. per sq. cm. (°C. per cm.) at 28.2°C. for wrought iron for which an iron content of 99.93 per cent was reported. A temperature coefficient of thermal conductivity of 0.0003 was given for this material. Hall, Campbell, Serviss, and Churchill[130] reported the same value, 0.1528 cal. per sec. per sq. cm. (°C. per cm.) for the thermal conductivity at 28.2°C. but a somewhat higher value, 0.00070, for the temperature coefficient between 13 and 87°C. Between 115 and 204°C. the temperature coefficient was 0.00068.

77. Recent Determinations of Thermal Conductivity.—The effect of temperatures up to 800°C. on the thermal conductivity
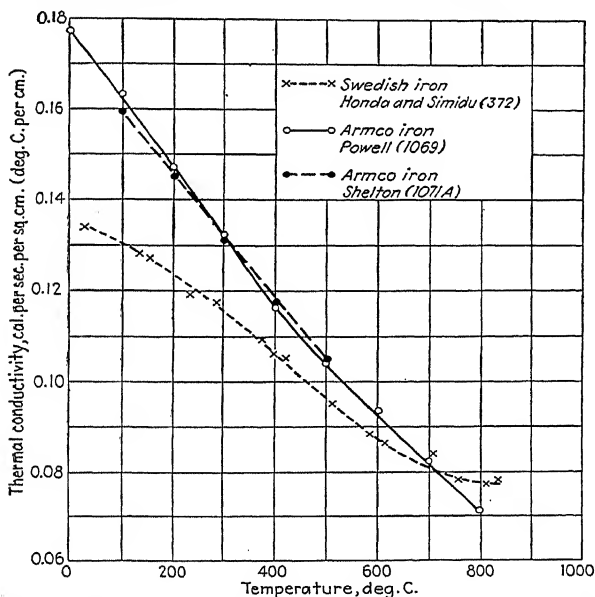
Fig. 20.—Effect of temperature on the thermal conductivity of iron.

of iron was reported by Honda and Simidu[372] for a sample of Swedish iron of unstated composition, and by Powell[1069] for a sample of Armco iron. Shelton[1071A] determined the thermal conductivity of Armco iron between 100 and 500°C.; his results are in excellent agreement with those of Powell for the same temperature range. Shelton remarked that the difference in

thermal conductivities of steels usually is less marked at high temperatures than at low temperatures; Powell called attention to the divergence of his results from those of Honda and Simidu at the lower temperatures and stated that this divergence would be discussed in a later publication.　Data from the three investigations are shown in Fig. 20.

The value 0.182 cal. per sec. per sq. cm. (°C. per cm.) was obtained by Sedström[581] on a vacuum-melted electrolytic iron, but Sedström stated that he did not consider the value reliable.　A similar value, 0.187 cal. per sec. per sq. cm. (°C. per cm.), was reported by Benedicks, Bäckström, and Sederholm[651] on iron containing 0.254 per cent of impurities.　Extrapolation to zero carbon, of results on a series of steels, gave 0.227 cal. per sec. per sq. cm. (°C. per cm.) for the thermal conductivity of carbon-free iron.　Powell[1069] recently reported that the thermal conductivity of a sample of high-purity iron which was prepared at the National Physical Laboratory was 0.185 cal. per sec. per sq. cm. (°C. per cm.) at 50°C. and, by extrapolation, 0.194 at 0°C.

The thermal conductivity of Armco iron wire at 0, −78.5, and −183°C. was determined by Kannuluik,[1008] as follows:

Temperature, °C.	Thermal Conductivity, cal. per Sec. per Sq. Cm. (°C. per Cm.)
0	0.169
− 78.5	0.171
−183	0.224

The thermal conductivities of three samples of vacuum-melted electrolytic iron, varying in grain size, were determined at 0° and −193°C. by Eucken and Dittrich.[710]　Their results converted to the usual units were as follows:

Average number of grains per linear cm.	Thermal conductivity, cal. per sec. per sq. cm. (°C. per cm.)	
	At 0°C.	At −193.1°C.
10	0.225	0.439
170	0.215	0.437
634	0.197	0.280

Grüneisen and Goens[716] did not detect any effect of grain size on thermal conductivity at low temperatures but found impurities to have a greater effect at low temperatures than at room temperature. Their results on the effect of impurities were:

Material	Thermal conductivity, cal. per sec. per sq. cm. (°C. per cm.)	
	At −190°C.	At −252°C.
Electrolytic iron No. 1 (purest).............	0.360	1.34
Electrolytic iron No. 2 (intermediate)........	0.325	0.719
Electrolytic iron No. 3 (least pure)...........	0.217	0.118

The effect of magnetization upon the thermal conductivity was reported by Brown[769] who found that a field of 4000 gausses decreased it about 0.4 per cent while a field of 8000 gausses had no detectable effect. The thermal conductivity of the iron used by Brown was 0.179 cal. per sec. per sq. cm. (°C. per cm.) at room temperature. Bridgman[431] studied the effect of pressure on the thermal conductivity of iron.

78. Summary of Data on Thermal Conductivity.—Selection of a value for the thermal conductivity of high-purity iron from the data available is largely a matter of opinion. The negligible amount of work existent and lack of agreement indicate the need for more precise data. The International Critical Tables[834] give 0.148 and the range of probable values as 0.136 to 0.160 cal. per sec. per sq. cm. (°C. per cm.). In view of later values of 0.197 to 0.225 reported by Eucken and Dittrich[710] for electrolytic iron, and of 0.194 reported by Powell[1069] for high-purity iron, selection of a somewhat higher value than 0.148 seems to be justified. The value 0.19 cal. per sec. per sq. cm. (°C. per cm.) is suggested as the best present approximation for the thermal conductivity of iron at 0°C. The data of Honda and Simidu,[372] of Powell,[1069] and of Shelton[1071A] are the only available representations of the change of thermal conductivity of fairly pure iron with temperature.

D. THERMAL EXPANSIVITY

The thermal expansion of iron has been the subject of considerable investigation, principally in connection with studies of its allotropy. The results of many investigations have been reported in the form of differential curves which have served to locate the transformation points but which are of little worth in obtaining values for the coefficient of thermal expansion. The dilatometry of iron as related to the study of the transformations was discussed in a previous section (p. 101).

The coefficient of linear thermal expansion is the increase in length of unit length for 1° rise in temperature, sometimes referred to in the literature as the "true coefficient of expansion" for that temperature. The average expansion per degree over a temperature range is termed the mean coefficient of expansion for that temperature range.

79. Thermal Expansivity of Alpha Iron at Low Temperatures. Values for the coefficient of linear thermal expansion at low temperatures were reported by Dorsey[155] for iron containing the following reported impurities: 0.058 per cent carbon, 0.008 per cent silicon, 0.071 per cent manganese, and a trace of phosphorus. Values were also given by Ebert[772] and Simon and Bergmann[906] for electrolytic iron. Their data are given in Fig. 21. The results of Dorsey and of Ebert are in fair agreement, but those of Simon and Bergmann are not in accord with the results of the other observers, particularly above −30°C. Ebert reports 11.1×10^{-6} per degree centigrade, and the value from Dorsey's curve is 11.5×10^{-6} per degree centigrade for the coefficient of linear thermal expansion at 0°C., but the value from the curve of Simon and Bergmann is 15.1×10^{-6}, which is more than 30 per cent higher than either of the other values. The data of Simon and Bergmann show an irregularity at about −50°C., which is not shown in the other curves in Fig. 21. However, recent work* with several samples of high-purity iron produced evidence of an irregularity in the expansion curve at about −50°C. although the effect is not so pronounced as that reported by Simon and Bergmann.

* Private communication from Dr. John Johnston, Director of Research, United States Steel Corporation.

Waggoner[201] determined the coefficients of expansion of a series of carbon steels between the temperature of liquid air and room temperature. By extrapolation he derived the value 9.28×10^{-6} per degree centigrade for the mean coefficient of linear expansion of carbon-free iron in this temperature range,
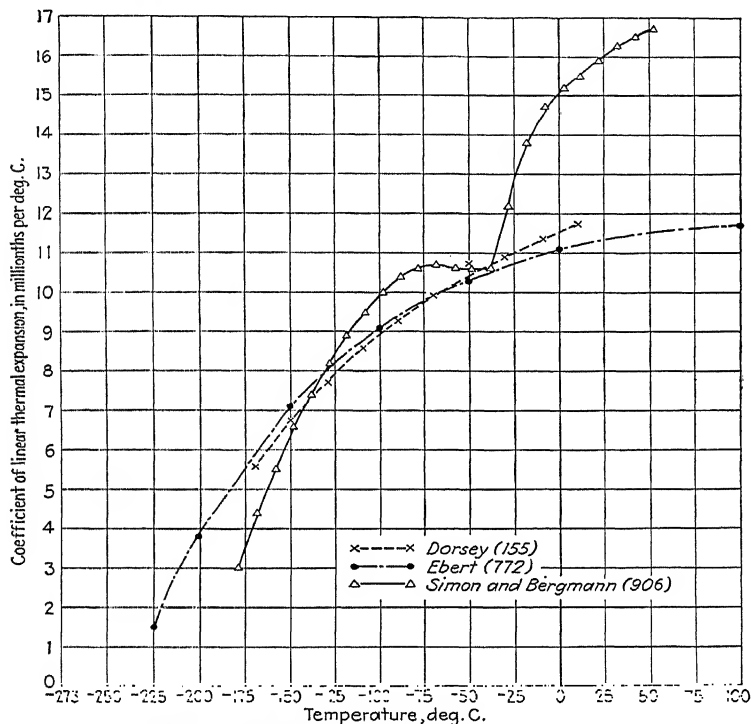
FIG. 21.—Coefficient of linear thermal expansion of iron at low temperatures.

an excellent agreement with Dorsey's value, 9.25×10^{-6} per degree centigrade.

80. Thermal Expansivity of Alpha Iron at Elevated Temperatures.—Investigators who have determined the coefficient of linear thermal expansion of iron at elevated temperatures by direct measurement include the following: Driesen,[279] Maurer and Schmidt,[441] Souder and Hidnert,[490] Sieglerschmidt,[905] and

Austin and Pierce.[1046]   Esser and Müller[997] and Schmidt[1028] calculated the thermal expansion coefficient of iron from X-ray data.   Driesen used iron containing 0.05 to 0.06 per cent carbon, 0.08 per cent manganese, 0.023 per cent sulphur, 0.03 per cent copper, and traces of silicon and phosphorus.   Esser and Müller used electrolytic iron and carbonyl iron.   Austin and Pierce
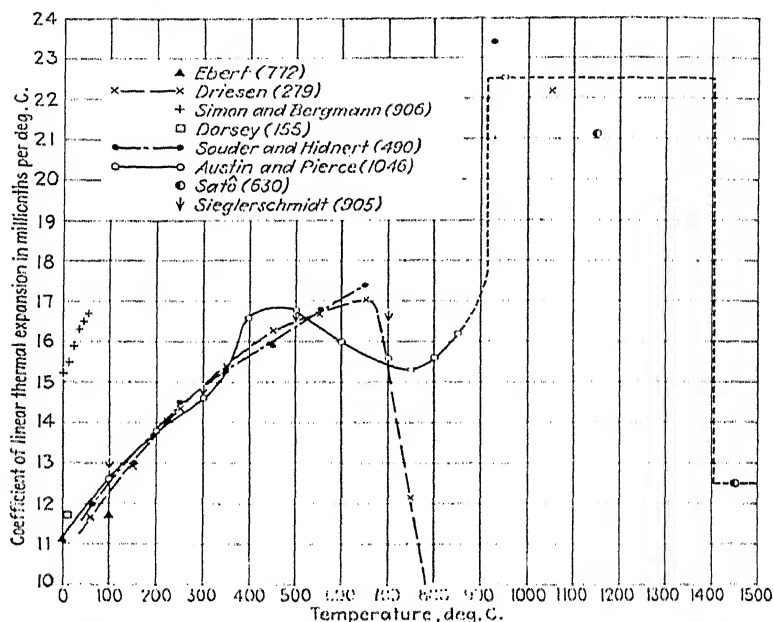
Fig. 22.—Coefficient of linear thermal expansion of iron at elevated temperatures.

made their measurements on ten specimens which included electrolytic iron, carbonyl iron, and ingot iron.   Some of Austin and Pierce's specimens were vacuum melted, some melted under hydrogen, and some annealed in hydrogen at 1500°C.   The other investigators used electrolytic iron.

The values for the mean coefficients of linear expansion of alpha iron obtained by these investigators are given in Table 20, those for the true coefficient in Table 21 and in Fig. 22. In plotting Fig. 22 the values of Driesen and of Souder and

TABLE 20.—MEAN COEFFICIENT OF LINEAR EXPANSION OF ALPHA IRON

Driesen[279] Temperature interval, °C	Mean coefficient, millionths per °C	Maurer and Schmidt[441] Temperature interval, °C	Mean coefficient, millionths per °C	Souder and Hidnert[190] Temperature interval, °C	Mean coefficient, millionths per °C	Esser and Muller[997] Temperature interval, °C	Electrolytic iron	Carbonyl iron	Schmidt[1023] Temperature interval, °C	Mean coefficient, millionths per °C	Austin and Pierce[1046] Temperature interval, °C	Mean coefficient, millionths per °C
20 to 100	11.66	20 to 50	11.30	25 to 100	12.0	20 to 50	.....	13.98	20 to 100	11.6	0 to 100	11.9
100 to 200	12.93	20 to 100	11.70	100 to 200	13.0	20 to 100	13.11	13.54	20 to 400	12.0	0 to 200	12.3
200 to 300	14.23	20 to 150	12.25	200 to 300	14.5	20 to 150	13.44	13.71	20 to 740	12.7	0 to 300	13.1
300 to 400	15.34	20 to 200	12.94	300 to 400	15.3	20 to 200	13.79	13.98	20 to 900	13.6	0 to 400	13.7
400 to 500	16.27	20 to 250	13.40	400 to 500	15.9	20 to 250	14.29	14.28	20 to 1400	16.2	0 to 500	14.4
500 to 600	16.64	20 to 300	13.71	500 to 600	16.8	20 to 300	14.73	14.48			0 to 600	14.7
600 to 700	17.03	20 to 350	13.94	600 to 700	17.4	20 to 350	15.04	14.67			0 to 700	14.9
700 to 800	12.12	20 to 400	14.15	25 to 300	13.3	20 to 400	15.36	14.81			0 to 800	14.9
800 to 900	−5.89	20 to 450	14.31	300 to 600	15.9	20 to 450	15.61	15.03				
				25 to 600	14.7	20 to 500	15.80	15.22				
						20 to 550	15.96	15.49				
						20 to 600	16.09	15.72				
						20 to 650	16.20	15.98				
						20 to 700	16.35	16.29				
						20 to 750	16.09	16.23				
						20 to 800	16.13	15.82				
						20 to 850	16.21	15.66				
						20 to 900	16.25	15.73				

Hidnert for the mean coefficient of linear expansion were plotted at the median temperature of the temperature intervals.

Table 21.— Coefficient of Linear Expansion of Alpha Iron

Temperature, °C.	Coefficient of linear expansion, millionths per °C.	
	Austin and Pierce[1046]	Sieglerschmidt[905]
100	12.6	12.9
200	13.8	
300	14.6	14.7
400	16.6	
500	16.8	16.5
600	16.0	
700	15.6*	16.5
750	15.3*	
800	15.6*	
850	16.2*	

* Averaged by the authors; see text below.

The results of Austin and Pierce[1046] led them to state that: "At higher temperatures there are considerable differences which indicate that in this region the expansion of a given sample of iron is sensitive to very small changes in composition or previous treatment or both. Consequently, a precise general coefficient cannot be given for pure alpha iron between 600°C. and the A_3 point." Austin and Pierce, therefore, did not give selected averages for the coefficient of linear expansion of alpha iron above 600°C., but the authors averaged the results of their three purest samples and included these average values in Table 21, along with the selected averages of Austin and Pierce for the lower temperatures. Because the values obtained on the different specimens at temperatures above 600°C. are not in good agreement, the averages of these values, as Austin and Pierce have stated, cannot be accepted as precise. They do serve, however, to indicate the coefficient of expansion versus temperature relation for high-purity iron at the higher temperatures.

The values for the mean coefficients of linear expansion derived by Schmidt[1028] from his X-ray data are lower, whereas the values of Esser and Müller,[997] also from X-ray data, are higher

than the values obtained by most investigators who used direct measurement methods.

81. Thermal Expansivity of Gamma Iron.—Values which have been reported for the coefficient of linear expansion of gamma iron are given in Table 22.

TABLE 22.—COEFFICIENT OF LINEAR EXPANSION OF GAMMA IRON

Investigator	Temperature interval, °C.	Coefficient of linear expansion, millionths per °C.	Method
Driesen[279]	900 to 1000	22.18	Direct measurement
Souder and Hidnert[490] .	906 to 945	23.4	Direct measurement
Satô[630]	900 to 1400	22.12	Direct measurement
Esser and Müller[997]			X-rays
Electrolytic iron	900 to 950	25.81	
Electrolytic iron	900 to 1000	25.53	
Electrolytic iron	900 to 1050	25.44	
Electrolytic iron	900 to 1100	25.53	
Carbonyl iron	900 to 950	24.14	
Carbonyl iron	900 to 1000	23.87	
Carbonyl iron	900 to 1050	23.96	
Carbonyl iron	900 to 1100	24.01	
Schmidt[1028]	920 to 1400	24.1	X-rays
Austin and Pierce[1046] . . .	. . . .	22.5	Direct measurement

The data obtained by direct measurement of the linear expansion of gamma iron are not sufficient to define the effect of temperature on the coefficient. The X-ray data of Esser and Müller indicate that the coefficient is constant between 900 and 1100°C.

82. Thermal Expansion of Delta Iron.—Satô[630] reported a value of 16×10^{-6} per degree centigrade for the coefficient of linear expansion of delta iron, approximately an extrapolation of that of alpha iron. Ralston[853] recalculated the coefficient from Satô's data and obtained 12.5×10^{-6} per degree centigrade. Calculation of the coefficient from Schmidt's[1028] X-ray data gives the value 19.5×10^{-6} per degree centigrade.

83. Thermal Expansion of Molten Iron.—Berlin[652] determined the density of molten iron at several different temperatures; from these densities the cubical expansion of molten iron

can be calculated. Berlin's value for the density of molten iron at the melting point is 7.4; at 1700°C. it is 6.9 g. per cu. cm. The coefficient of cubical expansion calculated from Berlin's data is 0.00043 per degree centigrade between the melting point and 1700°C. Benedicks, Ericsson, and Ericson[817] reported the specific volume of electrolytic iron as 0.1384 at the melting point and as 0.1397 at 1600°C. These data give the value 0.00014 per degree centigrade for the coefficient of cubical expansion of electrolytic iron between the melting point and 1600°C.

84. Thermal Expansion at the A_2 Point.—Investigators generally have failed to find any abnormality in the thermal expansion of iron at the A_2 point. Benedicks[297] found a slight deflection at 760 to 775°C. in the differential dilatometric curve of iron against gold, but this deflection was only 0.003 of that at the A_3 point. Chevenard[366] also noted a slight negative value for the differential expansion of electrolytic iron against Pyros metal at 765°C. As Chevenard's furnace was non-inductively wound, he did not consider the deflection a magnetostrictive effect as had been suggested by others. Ralston's[853] coefficient of expansion versus temperature curve showed the coefficient rising to a maximum at about 550°C. and then decreasing to the A_3 point, while the curve given in Abegg's Handbook[914] rises to a maximum at about 760°C. and then decreases to a minimum at the A_3 point, both curves representing selected averages of previous investigators. The work of Austin and Pierce[1046] indicated that the coefficient passes through a maximum near 450°C., then through a minimum at the A_2 point followed by an increase to the A_3 point. Coefficients derived by Esser and Müller[997] from their X-ray data agree with the results of Austin and Pierce.

85. Thermal Expansion at the A_3 Point.—A sudden contraction occurs as iron is heated through the A_3 range; conversely, an expansion occurs upon cooling through this range. Austin and Pierce[1046] found that the change in length differed greatly with different samples and that with the purest samples the expansion upon cooling exceeded the contraction upon heating. They cited other writers who had observed this permanent increase in length of specimens of high-purity iron when repeatedly heated and cooled through the A_3 transformation and concluded that "pure iron is not a suitable material for

measuring the change in macroscopic linear dimensions of iron at the A_3 inversion, since the change is neither reversible nor predictable." Souder and Hidnert[490] observed the opposite effect with their electrolytic iron: On heating and cooling through the alpha-gamma transformation, the contraction upon heating was greater than the expansion upon cooling, resulting in a permanent decrease in the length of the specimen. The variability in expansion and contraction at the inversion possibly accounts for the discrepancies in the values reported by the different investigators for the change in length at A_3, as follows:

Investigator	Linear Change at the A_3 Point, Thousandths $\Delta L/L$
Driesen[270]	1.9
Benedicks[207]	0.82
Chevenard[366]	2.2
Souder and Hidnert[490]	1.31 (heating)
	0.16 (cooling)
Satô[630]	2.82
Austin and Pierce[1046]	2.6
Calculated from the X-ray data of Schmidt[1028]	3.5
Calculated from the X-ray data of Esser and Müller[997]	3.8

The values ascribed to Schmidt and to Esser and Müller were calculated from values for the lattice constants of alpha and gamma iron obtained by extrapolation to 900°C. of their respective data. Austin and Pierce reported 2.6×10^{-3} as the value they derived from Schmidt's X-ray data. This was apparently obtained from Schmidt's lattice constants for 890 and 920°C. without extrapolation.

86. Thermal Expansion at the A_4 Point.—The change in the linear expansion at the A_4 point is positive; there is a sudden expansion during heating and a sudden contraction during cooling. The only direct determination available is that of Satô[630] which is given below with the values calculated by the authors from the X-ray data for gamma and delta iron:

Investigator	Linear Change at the A_4 Point, Thousandths $\Delta L/L$
Satô[630]	0.851
Calculated from X-ray data of Westgren and Phragmén[403]	3.2
Calculated from X-ray data of Bach[816]	2.6
Calculated from X-ray data of Schmidt[1028]	1.4

87. Volume Change at the Melting Point.—In view of the great discrepancies between the values of various investigators for the density of molten iron, values for the volume change at the melting point, calculated from these density values, are of little worth. Honda and Endo[722] calculated the volume change in "pure" iron during solidification as −4.4 per cent, based on extrapolation of Westgren's value for the lattice constant of delta iron and on Benedicks' value of 6.97 g. per cu. cm. for the density of molten iron. However, if the later value of Benedicks, Ericsson, and Ericson for the specific volume of iron at the melting point, 0.1384 cu. cm. per g. (corresponding to a density of 7.23 g. per cu. cm.), is used in the calculation, the volume change on freezing is found to be −0.94 per cent, whereas, if Berlin's value, 7.4 g. per cu. cm., is used for the density of molten iron at the melting point, the volume change on freezing appears to be +1.4 per cent.

88. Summary of Data on Thermal Expansivity.—The data of Dorsey[155] and of Ebert[772] for the coefficient of linear thermal expansion of iron at temperatures below 0°C. are in fair agreement. The iron used by Ebert was superior in purity to that of Dorsey, hence Ebert's values are preferred. The values of Simon and Bergmann[900] are not in accord with those of other investigators.

In the temperature range 0 to 600°C. the results of the various investigators are in fair agreement. The high purity of the specimens used by Austin and Pierce[1046] and the probable sensitivity of their apparatus (the vacuum interferometer) seem to justify selection of their data as the most probable. The results of Austin and Pierce for alpha iron above 600°C. vary considerably from those obtained by other investigators who used direct measurement methods. Whether this variance is due to the higher purity of the specimens used by Austin and Pierce or is a result of some peculiarity of their apparatus cannot be readily judged. Until the results of Austin and Pierce are confirmed or disproved, the dilatometric behavior of high-purity iron between 600°C. and the A_3 point is conjectural.

The value 22.5×10^{-6} per degree centigrade, obtained by Austin and Pierce[1046] for the coefficient of linear thermal expansion of gamma iron, is approximately an average of the other values obtained by direct measurement. The X-ray data

of Esser and Müller[997] and Schmidt[1028] indicate that the thermal expansion coefficient of gamma iron is constant between the A_3 and A_4 points.

The value of 2.6×10^{-3} reported by Austin and Pierce for the change in length at the A_3 point is approximately an average of the available data for high-purity iron. The available information on the thermal expansion of delta and molten iron, on the change in length at the A_4 point, and on the volume change at the melting point is so inadequate that a selection of probable values is impossible.

E. AUTHORS' SUMMARY

Some of the thermal properties of iron can be stated in numerical terms, others are conveniently expressed in the form of curves. In some cases there are not enough data available to justify a selection.

It is suggested that 1535°C. (2795°F.) be accepted as the best present approximation of the melting point of high-purity iron and that 3000°C. (5430°F.) be accepted as the corresponding value for the boiling point. The vapor pressure of iron is very small at all temperatures below the melting point, according to the data in Table 11 (p. 134) but, according to Kelley[1078], increases rapidly with increasing temperature above this point.

The values which have been selected for the various phases of the heat capacity of iron are taken chiefly from the critical reviews of Austin.[955,956] Figure 18 (p. 146) summarizes Austin's results for the specific heat of iron between absolute zero and 1600°C. (−460 and 2910°F.). There is probably no heat effect accompanying the A_2 transition. Klinkhardt's[725] value, 3.86 cal. per g. (216 cal. per g. atom), and Ralston's[853] value, 1.7 cal. per g. (95 cal. per g. atom), are selected for the heat effects of the A_3 and A_4 transformations respectively. The value 65 cal. per g. (3630 cal. per g. atom) is suggested as the best present approximation for the heat of fusion of iron. The data of Austin[956] for the entropy, heat content, and free energy of iron over a wide range of temperature are given in Tables 18 and 19 (pp. 152, 153). For temperatures below the A_2 point, the form of the heat capacity versus temperature curve has been established, but the different investigators are not in agreement in regard to the numerical values. However, as Austin[955] pointed out,

the accuracy of the best data for this temperature range is probably sufficient for practical purposes. Above the A_2 point both the form of the curve and the numerical values are controversial. The doubtful accuracy of the data for specific heat at high temperatures naturally affects the related data for heat content, free energy, and entropy. The available data show clearly that further work on the thermal properties, particularly of gamma and delta iron, is necessary.

The few data which are available for the thermal conductivity of high-purity iron indicate that 0.19 cal. per sec. per sq. cm. (°C. per cm.) is the most probable value for this property at 0°C. The effect of temperature on the thermal conductivity is shown in Fig. 20 (p. 155).

Available data for the thermal expansivity of iron from −225 to 1500°C. (−375 to 2730°F.) are summarized in Figs. 21 and 22 (pp. 159, 160). The irregularity at about −50°C. (−60°F.), which was shown by the data of Simon and Bergmann,[906] has been confirmed by recent work although the confirmation is qualitative, not quantitative. There is no expansion or contraction accompanying the A_2 transition. When iron is heated through the A_3 range a contraction occurs; conversely an expansion occurs on cooling. The amount of this change varies with different specimens, and expansion and contraction of the same sample are not necessarily equal. The change in linear expansion at the A_4 point is in the reverse direction to that of the change at the A_3 point. The change from gamma to delta iron is accompanied by an expansion, the reverse change by a contraction. The solidification of molten iron is accompanied by a contraction in volume, but the amount of this contraction, for high-purity iron, has been determined only by calculations based on density data. The density of high-purity iron has not been accurately determined at temperatures near the melting point; consequently, the calculated values for the solidification shrinkage vary from about 1 to 5 per cent, depending upon the selected densities on which the calculations are based.

Accurate determination of the thermal properties of high-purity iron, at all temperatures but particularly at temperatures above 500 or 600°C. (930 or 1110°F.), is a subject for future investigations.

CHAPTER VI

ELECTRIC PROPERTIES

Resistivity—Thermal Electromotive Force—Peltier Effect—Thomson Effect—Authors' Summary

Mention of the electric properties of a metal suggests discussion of the conductivity or of the reciprocal property, resistivity. Metallic elements in general are conductors of electricity but differ widely in their capacities in this respect. The conductivity of iron is appreciably lower, and the resistivity is higher, than the corresponding properties of copper, for example. Iron has found some use as a constituent of resistance alloys, but the principal interest in the resistivity of iron is in relation to the magnetic characteristics of the metal.* The thermoelectric properties, which include the thermal electromotive force, and the allied phenomena of Peltier and Thomson effects, are of scientific rather than of technical importance, with the exception that the thermocouple of iron and constantan is extensively used in industry.

Determinations of the electric properties as well as other properties of iron at different temperatures have been used in the study of the allotropy of iron. This subject was discussed in a preceding chapter.

A. ELECTRIC RESISTIVITY

The electric resistivity of metals is greatly influenced by the presence of impurities and to a lesser extent by the thermal and mechanical treatments to which the metal has been subjected. Even with the influence of these variables added to the experimental errors, the agreement of the reported values for the electric resistivity of iron is not so good as might be expected.

* A considerable tonnage of low-carbon (less than 0.10 per cent) basic open-hearth steel, both ordinary and rephosphorized, is used as a conductor in telephone and telegraph circuits. The best grade of this wire has ten to twelve times the resistance at room temperature of copper wire of the same cross section.

In the ensuing discussion of resistivity, values for the temperature coefficient of resistance also will be considered. This function for solid iron is the ratio of the change in resistance per degree over the temperature interval to the resistance at 0°C, according to the equation:

$$\text{Temperature coefficient, } \alpha = \frac{R_t - R_{t'}}{R_0(t - t')}$$

where R_t, $R_{t'}$, and R_0 are the resistances at temperatures t, t', and 0°C. All the values for the temperature coefficient which are used in this monograph have been computed according to this equation. In the few cases where investigators have reported temperature coefficients which were obtained by other formulas, the values ascribed to these investigators in this review have been computed from their resistance data according to the accepted formula. The temperature coefficient for the temperature range from 0 to 100°C. is termed the fundamental coefficient. This value, according to information available at present, increases with increasing purity of the metal and, therefore, serves in many cases as an indication of the comparative purity of the specimens which were used in different investigations. For this reason, values for the fundamental coefficient are included, if available, in the discussion of resistivity values in preference to reviewing them in a separate section.

89. Early Work on Resistivity at Low Temperatures.—Of the iron specimens used by Dewar and Fleming[56] in their classic work on the low-temperature properties of materials, only the

TABLE 23.—RESISTANCE OF "H W IRON" AT LOW TEMPERATURES*

Temperature		Resistivity, microhm-cm.	Ratio, R_t/R_0
°K.	°C.		
273.2	0	9.065	1.000
234.0	− 39.2	7.168	0.791
191.3	− 81.9	5.318	0.586
76.1	−197.1	1.220	0.135
54.2	−219.0	0.725	0.080
51.0	−222.2	0.660	0.073
50.8	−222.4	0.649	0.072
50.5	−222.7	0.644	0.071

* Dewar and Fleming.[56]

"H W iron," results of which are recorded in Table 23, appears to have been of sufficient purity* to warrant consideration in the present review. Dewar and Fleming observed that the purer the metal the closer the approach to zero resistance at absolute zero of the (extrapolated) resistivity-temperature curve. They surmised that with perfect purity metals would have no resistance or at most an extremely small residual resistance at absolute zero.

The low-temperature resistance values obtained by Niccolai[182] on Kahlbaum iron are considerably higher than those reported by other investigators. Niccolai found that the ratio of resistance at $-189°C$. to that at $0°C$. was 0.249, whereas Schimank[315] reported the R_t/R_0 ratio for Kahlbaum iron as 0.1033 at $-192.6°C$., and Holborn[400] gave the ratio as 0.0848 at $-192.7°C$., also for Kahlbaum iron. The data of Schimank[315] given in Table 24 were obtained on annealed Kahlbaum iron and on unannealed Heraeus electrolytic iron. Schimank made the first measurements of the electric resistance of iron at the temperature of liquid hydrogen.

TABLE 24.—RESISTANCE OF IRON AT LOW TEMPERATURES*

Kahlbaum iron, annealed			Heraeus iron, unannealed		
Temperature		R_t/R_0	Temperature		R_t/R_0
°K.	°C.		°K.	°C.	
273.2	0	1.000	273.2	0	1.000
197.8	− 75.4	0.6130	198.3	− 74.9	0.6148
80.6	−192.6	0.1033	80.6	−192.6	0.1088
20.4	−252.8	0.0280	20.4	−252.8	0.0330

* Schimank.[315]

The data in International Critical Tables† for the resistance of iron at low temperatures are those of Holborn[400] for Kahlbaum nitrate iron, which was stated to contain 0.001 per cent manganese, 0.004 per cent copper, 0.004 per cent nickel and cobalt, and traces of other elements. Resistance values reported by Holborn for two samples of Heraeus vacuum-melted electrolytic

* See p. 175 for note on the purity of Dewar and Fleming's specimen.
† Volume 6, p. 127.

iron were somewhat higher than those obtained on the nitrate iron; temperature coefficient values for electrolytic iron I and for Kahlbaum iron were:

Temperature interval, °C.	Temperature coefficient × 100	
	Electrolytic iron I	Kahlbaum iron
0 to − 78	0.5322	0.5392
−78 to −195	0.4247	0.4311

The presumption therefore is that the latter was the purer material. Holborn's data on the three materials are given in Table 25.

TABLE 25.— RESISTANCE OF IRON AT LOW TEMPERATURES*

Electrolytic iron I			Electrolytic iron II			Kahlbaum iron		
Temperature		R_t/R_0	Temperature		R_t/R_0	Temperature		R_t/R_0
°K.	°C.		°K.	°C.		°K.	°C.	
273.2	0	1.000	273.2	0	1.000	273.2	0	1.000
194.8	− 78.4	0.5828	194.9	− 78.3	0.5838	195.1	− 78.1	0.5786
80.7	−192.5	0.0982	81.0	−192.2	0.0990	80.5	−192.7	0.0848
....	......	....	....	......	....	20.2	−253	0.0113

* Holborn.[400]

90. Recent Work on Resistivity at Low Temperatures.— Ribbeck[684] reported the specific resistance of electrolytic iron as 5.0 microhm-cm. at −78°C. and 0.8 microhm-cm. at −185°C. The R_t/R_0 ratio was 0.56 at −78°C. and 0.09 at −185°C. Three sets of values for the resistivity of electrolytic iron were reported by Grüneisen and Goens.[716] Whether the considerable difference in these three sets was due solely to the different mechanical and heat treatments of the specimens and, therefore, to the crystal size, or to a difference in chemical composition is not clear from the paper. The data of Grüneisen and Goens are given in Table 26.

TABLE 26.—RESISTANCE OF IRON AT LOW TEMPERATURES*

Temperature		Electrolytic iron I, double-deposited, worked, and annealed		Electrolytic iron II, polycrystalline, not annealed		Electrolytic iron III, large crystals, worked, annealed for 1 hr. at 500°C.	
°K.	°C.	R_t/R_0	Resistivity, microhm-cm.	R_t/R_0	Resistivity, microhm-cm.	R_t/R_0	Resistivity, microhm-cm.
273.2	0	1.000	8.71	1.000	9.11	1.000	9.95
83.2	−190	0.0893	0.778	0.1020	0.929	0.193	1.917
21.2	−252	0.0078	0.068	0.0158	0.144	0.1065	1.060

* Grüneisen and Goens.[716]

Two investigations were reported by Meissner, in 1926[678] and 1929,[847] but the latter is so much superior as to warrant limiting consideration to the 1929 data, reproduced in Table 27. Meissner carried his investigation of the resistance of iron to 1.30° absolute (−272°C.) and found no indication of superconductivity, thereby confirming the observation of Tuyn and Onnes.[744] It will be seen from inspection of Meissner's data that a minimum resistance, different for each iron, was reached at about −269°C., no further decrease in resistance occurring with decrease in temperature. Whether this residual resistance is a property of the iron itself or is a result of the presence of impurities in the specimens will be determined by investigation of iron of higher purity.

91. Summary of Resistivity at Low Temperatures.—As the evidence appears conclusive that the R_t/R_0 ratio for a metal at temperatures below 0°C. becomes lower with increasing purity of the metal, there seems to be justification for the selection of the lowest set of values, those obtained by Meissner on the Griesheim electrolytic iron, as the most probable for the low-temperature resistivity of pure iron. The resistivity-temperature curve (Fig. 23) was plotted from these values with the inclusion of Holborn's value, 0.5786 at −78.1°C. as an intermediate point.

92. Early Data on Resistivity between 0° and 100°C.—The earliest value for the resistivity of "pure" iron seems to be that of Preece,[38] reported in 1887. The materials used were com-

TABLE 27.— RESISTANCE OF IRON AT LOW TEMPERATURES*

Temperature		Ratio, R_t/R_0			
°K.	°C.	Holbrook nitrate iron	Kahlbaum iron, annealed	Griesheim electrolytic iron, annealed	Heraeus electrolytic iron, worked, large crystals
273.20	0	1	1	1	1
83.91	−189.29	0.1002	0.0952		
78.25	−194.95	.....	.....	......	0.0756
78.21	−194.99	.....	.....	0.0741	
20.39	−252.81	.....	.....	0.00761	0.00892
20.38	−252.82	0.0151	0.0112		
4.22	−268.98	.....	.....	0.00620	0.00818
4.21	−268.99	0.0141			
3.71	−269.49	0.0141			
1.98	−271.22	.....	0.0102	0.00618	0.00819
1.30	−271.90	0.0141	0.0103		

Temperature		Ratio, R_t/R_0				
		Kreusler iron		Siemens and Halske iron		Electrolytic iron, annealed 3 hr. at 300°C. (570°F.), etched
°K.	°C.	Un-treated	Annealed 3 hr. at 300°C. (570°F.)	Un-treated	Annealed 3 hr. at 300°C. (570°F.)	
273.20	0	1	1	1	1	1
90.47	−182.73	.....	.....	0.1734	0.1496	
81.74	−191.46	.....	.....	0.1482	0.1240	0.1220
77.75	−195.45	0.0850	0.0822			
20.44	−252.76	.....	.....	0.0670	0.0436	0.0414
20.42	−252.78	0.0181	0.0163			
4.23	−268.97	.....	0.0154	0.0644	0.0420	0.0390
4.22	−268.98	0.0164				
3.71	−269.49	.....	0.0151	0.0643	0.0419	0.0390
1.38	−271.82	.....	0.0150	0.0643	0.0419	0.0390
1.35	−271.85	0.0163				

* Meissner.[847]

mercial irons, the purest a Swedish iron having a resistivity of 9.907 microhm-cm. at 14°C. By extrapolation to zero impurities Preece derived the value 9.753 microhm-cm. for the resistivity of pure iron at 14°C. A much higher value, 11.9 microhm-cm., presumably at room temperature, was reported the following year by Kohlrausch[43] as the resistivity of an electrolytic iron prepared by the Klein process. Dewar and Fleming [56] obtained a resistivity of 9.07 microhm-cm. at 0°C. for a specimen of iron,
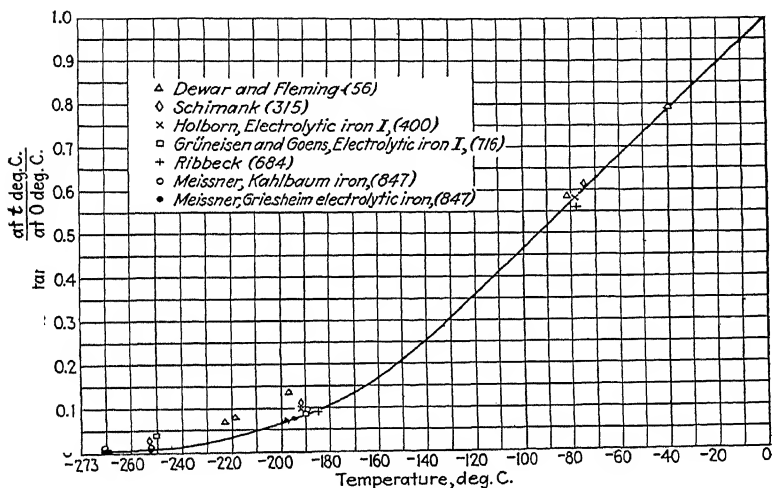
Fig. 23.—Electric resistance of iron at low temperatures.

designated "H W iron," which seems to have been rather pure as judged by the fundamental coefficient, 0.00625 per degree. The fundamental coefficient for basic open-hearth ingot iron containing 0.13 to 0.15 per cent of impurities is about 0.0061. The "H W iron" used by Dewar and Fleming apparently was of somewhat higher purity than basic open-hearth ingot iron.

The value 7.6 microhm-cm. at 16°C., proposed by Benedicks[107] for the resistivity of pure iron, was obtained from that of impure iron by an extrapolation based on the assumption that atomically equivalent amounts of different elements present in iron cause equal increases in the resistivity. This hypothesis has been shown to be erroneous by Portevin,[199,310] Norbury,[417] and

others.   Portevin, repeating Benedicks' work, found that extrapolation to zero impurities for a series of steels gave 9.3 microhm-cm. at 20°C., a more probable value for the resistivity of pure iron.   The results obtained by extrapolation to zero impurities, although not strictly reliable, nevertheless furnish at least a qualitative indication of the merits of the results for resistivity.   The question is discussed in more detail in a later section of this chapter.

The resistivity of the supposedly pure iron prepared by Kreusler[180] in 1908 by ignition and reduction of precipitated ferrous oxalate was 9.4 microhm-cm. at 0°C.   In the same year Niccolai[182] reported the resistivity of Kahlbaum reduced iron, produced from ferrous oxalate, to be 10.68 microhm-cm. at 0°C.   The fundamental coefficients of the two materials, 0.0055 per °C. for the Kreusler iron and 0.00557 for the Kahlbaum iron, indicated that they were of about the same degree of purity, in contrast to the marked difference in the values for the resistivities.   The Physikalisch-Technische Reichsanstalt[186] in 1908 also reported the fundamental coefficient of Kahlbaum iron as 0.0055 and the resistivity at 18°C. as 10.4 microhm-cm. which at 0°C. would be about 9.4 microhm-cm.   The resistivity reported by the Reichsanstalt for iron prepared by ignition and reduction of recrystallized ferric nitrate was 10.0 microhm-cm. at 18°C. The fundamental coefficient between 0° and 100°C. being 0.0059 per degree centigrade, the resistivity at 0°C. would be about 9.05 microhm-cm.   The analyses reported by the Reichsanstalt were:

| | Percentage | |
Element	Kahlbaum iron (from oxalate)	Nitrate iron
Manganese	0.025	0.001
Copper....	0.03	0.004
Nickel.....	0.06	0.004
Carbon....	Trace	Trace
Silicon.....	Trace	Trace

The fundamental coefficients indicate considerably lower purity than is shown by the analyses.   Presence of considerable oxygen would be expected in reduced iron not melted under hydrogen.

93. Recent Data on Resistivity between 0 and 100°C.—A vacuum-melted electrolytic iron stated to have an iron content of 99.983 per cent was reported by Wenner and Lindberg*[834] to have a resistivity of 9.78 microhm-cm. at 20°C. In 1918 Gumlich[387] reported a number of values; two values, 9.74 and 9.92 microhm-cm. at 20°C., were for Fischer electrolytic iron, the remainder were obtained by extrapolating to zero impurities the resistivities of a series of irons and steels. The values obtained by extrapolation were all higher than the measurements on electrolytic iron, an indication of the unreliability of extrapolation as a method of obtaining the resistivity of pure iron.

Several values for electrolytic iron are found in the reports of Yensen's investigations of electric and magnetic properties. In 1914[321] he reported the average resistivity of 15 samples as 9.96 microhm-cm. at 20°C. The following year[342] two values, 9.82 and 9.85 microhm-cm. at 20°C., were obtained on electrolytic iron containing 0.01 per cent carbon and 0.01 per cent silicon. In 1924,[590] resistivities of from 9.91 to 10.25 microhm-cm. at 20°C. were obtained on electrolytic iron with an average of 0.045 per cent of reported impurities. Extrapolation to zero impurities gave 9.6 microhm-cm. as the resistivity of pure iron at 20°C.

The resistivity of basic open-hearth ingot iron stated to contain 0.075 per cent of impurities, exclusive of oxygen, was determined by Campbell[365] as 10.64 microhm-cm. at 25°C. The fundamental coefficient was 0.0060. Campbell and Mohr[653] obtained 10.44 microhm-cm. for the resistivity of ingot iron and, by extrapolation, 10.0 microhm-cm. for the resistivity of pure iron at 25°C. Powell[1069] found that the resistivity of ingot iron was 9.6 microhm-cm. at 0°C. and 15 microhm-cm. at 100°C. The fundamental coefficient for this material was 0.0056 per degree centigrade, a value which is appreciably lower than that ordinarily obtained for Armco iron. Electrolytic iron, after treatment in hydrogen for seven days at 950°C. to remove carbon, had a resistivity of 10.02 microhm-cm. at 25°C. as reported by Campbell.[599]

The only impurities detected in the electrolytic iron used by Yamada[696] were carbon and sulphur, the reported amounts of each being 0.006 per cent. This iron had a resistivity of 9.99

microhm-cm. at 20°C.   By extrapolation of the resistivities of a series of low-carbon steels, the value 10.12 microhm-cm. was obtained as the resistivity of pure iron at 20°C.

A specimen of annealed electrolytic iron prepared by a double electrodeposition had a resistivity of 8.71 microhm-cm. at 0°C. as determined by Grüneisen and Goens.[716]   Their results on two other electrolytic irons were 9.11 and 9.95 microhm-cm. at 0°C. The resistivity reported by Sedström[581] in 1924 for Heraeus electrolytic iron, 11.6 microhm-cm. at 0°C., is higher than most investigators have obtained on high-purity iron.   The same is true of the value reported in 1929 by Sizoo and Zwikker,[861] 10.3 microhm-cm. at 0°C., also obtained on Heraeus electrolytic iron.   The fundamental coefficients 0.00526 per degree centigrade for the iron used by Sedström and 0.0058 per degree centigrade for the iron used by Sizoo and Zwikker, indicate that inferior purity may be the explanation of the high resistivities.   The reported data of the resistivity and fundamental coefficient of iron between 0 and 100°C. are given in Table 28.

94. Summary of Resistivity between 0° and 100°C.—The values for the resistivity of iron at 20°C. which seem most likely to be precise are those obtained by Gumlich, 9.74 and 9.90 microhm-cm., and by Wenner and Lindberg, 9.78 microhm-cm. A rounded value of 9.8 microhm-cm. is suggested as the best present approximation for the resistivity of iron at 20°C.

Although an average of the best values for the fundamental coefficient of iron would be under 0.0065 per degree centigrade considerable weight must be given to the value 0.00657 per degree centigrade reported by Holborn and by Meyer.   A rounded value of 0.0065 per degree centigrade is suggested as the best present approximation for the fundamental coefficient of iron.

95. Early Data on Resistivity at High Temperatures.— Investigations of the resistivity of iron at high temperatures have had one or both of two ends in view: the determination of critical ranges by electric-resistance methods and the determination of the effect of temperature on the resistivity of iron.   The first phase of the subject has been discussed in the section on the allotropy of iron (Chapter IV); only the investigations of the variation of resistivity with temperature are reviewed here.

The determination by Morris[75] in 1897 of the resistivity of Swedish transformer iron between 0 and 1100°C. (32 and 2010°F.) is probably the earliest investigation in which a material of fair purity was used. The value of the fundamental coefficient for the iron, 0.0060 per degree centigrade, as derived from Morris' data, is the sole criterion of the purity of the material, no analysis being given. The resistivity of the iron at 0°C. was 10.05 microhm-cm. The values found by Niccolai[182] for the resistivity of Kahlbaum iron are in fair agreement with those of Morris between 100 and 400°C. (210 and 750°F.), the highest temperature to which Niccolai carried his measurements.

Three types of high-purity iron were used in an investigation by Meyer:[246] Kahlbaum reduced iron prepared from ferric nitrate, basic open-hearth ingot iron, and Langbein-Pfanhauser electrolytic iron. The basic open-hearth ingot iron was stated to have an iron content of 99.94 per cent but the oxygen content was apparently neglected in arriving at that figure. The impurities found in the Kahlbaum iron and in the electrolytic iron were:

Element	Percentage	
	Kahlbaum iron	Electrolytic iron
Carbon...................	.....	0.00
Copper..................	0.004	0.00
Sulphur.................	Trace	<0.008
Manganese..............	0.001	0.00
Silicon..................	0.015	0.00
Phosphorus.............	.....	0.007
Nickel..................	0.004	
Total..................	0.024	0.015

Meyer's results seem somewhat erratic in that the low resistivity of 8.53 microhm-cm. was obtained on the Kahlbaum iron at 0°C. as compared with 9.35 microhm-cm. for the electrolytic iron of about the same degree of purity, and 9.57 microhm-cm. for the basic open-hearth ingot iron. On nitrate iron, similar in composition to the Kahlbaum iron used by Meyer, the Physikalisch-Technische Reichsanstalt[186] obtained the previously mentioned

TABLE 28.—ELECTRIC RESISTIVITY AND TEMPERATURE COEFFICIENT OF RESISTANCE OF IRON BETWEEN 0 AND 100°C.

Investigator	Year	Material Source	Reported impurities, per cent	Temperature, °C.	Resistivity, microhm-cm.	Fundamental coefficient, ohms per °C. per ohm at 0°C.	Resistivity at 0°C., microhm-cm.
A. Electrolytic iron							
Kohlrausch[44]	1888	Klein-process electrolytic iron	....	Not given	11.9		
Meyer[240]	1911	Langbein-Planhauser electrolytic iron	0.015	0	9.35	0.00657	9.35
Yensen[331]	1914	Burgess-process electrolytic iron	0.0125 C	20	9.96		
Yensen[347]	1915	Burgess-process electrolytic iron	0.006 to 0.01 C and 0.01 Si	20	9.84		.
Wenner and Lindberg[334]	1915	....	0.017	20	9.78	0.00635	8.8
Saldau[335]	1916	....	0.047	25	10.95	0.0063	9.6
Gumlich[337]	1918	Fischer electrolytic iron	....	20	9.74	0.00579 at 20°C.	8.72
Gumlich[337]	1918	Fischer electrolytic iron	....	20	9.92	0.00575 at 20°C.	8.90
Sedström[551]	1924	Heraeus iron	....	0	11.6	0.00526	11.6
Yensen[339]	1924	....	....	20	9.91		
Campbell[499]	1925	Yensen electrolytic iron	....	25	10.02		
Yamada[564]	1926	....	0.006 C and 0.006 S	20	9.99		
Ribbeck[441]	1926	....	0.021	20	10.1	0.0064	8.9
Holborn[499]	1919	....	....	......	......	0.00657	
Grüneisen and Goens[546]	1927	From double electrodeposition	....	0	8.71		8.71
Sizoo and Zwikker[551]	1929	Heraeus electrolytic iron	....	0	10.3	0.0058	10.3
B. Reduced iron							
Kreusler[180]	1908	Iron from ferrous oxalate	....	0	9.4	0.0055	9.4

Niccolai[382]	1908	Kahlbaum iron (from oxalate)	....	0	10.68	0.00557	10.68
Physikalisch-Technische Reichs-anstalt[198]	1908	Iron from oxalate	0.115	18	10.4	0.0055	9.4
	1908	Iron from nitrate	0.019	18	10.0	0.0059	9.05
Meyer[246]	1911	Kahlbaum iron (from nitrate)	0.024	0	8.53	0.00821	8.53
Saldau[353]	1916	Kahlbaum iron	....	25	10.46	....	9.2
Holborn[400]	1919	Kahlbaum iron	....	:	.....	0.00648	.....
Powell[1089]	1934	Iron from chloride	....	50	11.45	....	8.8

C. Commercially pure iron

Preece[38]	1887	Swedish iron	No analysis	14	9.907	0.0048	9.28
Dewar and Fleming[56]	1893		No analysis	0	9.07	0.00625	9.07
Morris[76]	1897	Transformer iron	No analysis	0	10.05	0.0057	10.05
Barrett, Brown, and Hadfield[100]	1902	Swedish charcoal iron	0.11	18	10.2	.....	.....
Somerville[224]	1910	Commercial iron wire	....	:	9.57	0.0057	9.57
Meyer[246]	1911	Basic open-hearth ingot iron	0.06	0	9.57	0.00607	9.57
Honda and Simidu[272]	1917	Swedish iron	....	30	15.3	....	13.2
Campbell[365]	1917	Basic open-hearth ingot iron	0.075	25	10.64	0.0060	9.32
Bridgman[347]	1917	Basic open-hearth ingot iron	....	:	.....	0.0062	.....
Campbell and Mohr[653]	1926	Basic open-hearth iron	0.10	25	10.44	....	.....
Powell[1089]	1934	Basic open-hearth ingot iron	0.082	:	.....	0.0056	9.6

D. By extrapolation to zero impurities

Preece[38]	1887	....	14	9.753		
Benedicks[107]	1902	....	16	7.6		
Portevin[310]	1914	....	20	9.3		
Yensen[590]	1924	....	20	9.6		
Campbell and Mohr[653]	1926	....	25	10.0		
Yamada[690]	1926	....	20	10.12		
Gumlich[387]	1918	....	20	9.98		
Ribbeck[884]	1926	....	20	9.62		

resistivity of 10.0 microhm-cm. at 18°C. or about 9.05 at 0°C. Meyer also reported 0.00821 for the fundamental coefficient of the Kahlbaum iron, whereas the Reichsanstalt value was 0.0059. Meyer reported fundamental coefficients of 0.00607 per degree centigrade for the basic open-hearth ingot iron and of 0.00657 for the electrolytic iron. The latter value is identical with the value reported later by Holborn[400] for electrolytic iron. The considerable discrepancies between the results of Meyer on the Kahlbaum iron and those of other investigators on similar material indicate the presence of experimental errors sufficient to justify the exclusion of his data for that material from consideration in arriving at probable values for pure iron. Meyer's results on electrolytic iron and basic open-hearth ingot iron are more in line with those of other investigators. However, the slope of the temperature-resistance curve for each of his three irons reaches a maximum at about 700°C. (1290°F.) whereas all other investigators have obtained the maximum value at temperatures above 750°C. (1380°F.). This indicates that Meyer's temperature measurements may have been erroneous.

96. Recent Data on Resistivity at High Temperatures.— Kahlbaum iron was also used by Honda and Ogura[306] in their investigation of the temperature-resistance relation of iron between 18 and 1015°C. (65 and 1860°F.). A discontinuity in their curve at the A_2 point was due to insufficient points in the A_2 range, the earlier work of Morris[75] and the later work of Burgess and Kellberg[326] indicating a smooth curve at that point. The results of Honda and Ogura were reported as resistance of the particular wire used, but as the dimensions of the wire were given a rough calculation of the resistivity can be made. The values so obtained are much higher than have been reported by other investigators, particularly in the lower temperature ranges.

The purpose of the investigation by Burgess and Kellberg[326] was the determination of the form of the resistance-temperature curve of iron over the A_2 and A_3 ranges. The resistance measurements were made on electrolytic iron (reported impurities 0.02 per cent) in the form of a resistance thermometer; temperatures were determined by a platinum resistance thermometer encased with the iron. The results were reported as resistance in ohms of an iron wire of unstated dimensions, not, as was

assumed by Ralston,[853] as resistivity. The investigation, although of value in defining accurately the form of the resistance-temperature curve of iron, does not give information as to the resistivity. However, the resistivity of a specimen of the same iron was determined by Wenner and Lindberg[834]* to be 9.78 microhm-cm. at 20°C. The resistance at 20°C. of the wire used by Burgess and Kellberg can be found by interpolation on their curve extended to include their values for the resistance of the wire at 0 and 100°C.; the value so obtained by the authors of this monograph is 1.078 ohms. Their resistance values can then be converted to resistivity by multiplication by 9.78/1.078. The values credited to Burgess and Kellberg in Table 29 were obtained in this manner. The resistance measurements of Burgess and Kellberg between 250 and 950°C. (480 and 1740°F.) were carried out with precision, using temperature intervals of 2 to 3°C. Hence, their curve shows the temperature-resistance relations of their iron above 250°C. with considerable exactness. The resistivity values computed from the Burgess-Kellberg data are less precise, as the value selected for the resistance of their iron at 20°C. depends upon the form of the extrapolated temperature-resistance curve, which is defined below 250°C. only by the points at 0 and 100°C.

Burgess and Kellberg found that the resistance of their iron was slightly lower on cooling than on heating, which they ascribed to a difference in the rates of heating and of cooling. However, the data of Saldau[355] show the reverse, the iron during cooling having a considerably higher resistance than during heating. In Saldau's data, the resistivity of Kahlbaum iron at 25°C. was increased from 10.457 to 10.920 microhm-cm. by heating to 1100°C. (2010°F.) while the resistivity of electrolytic iron was increased from 10.949 to 11.484 microhm-cm. by similar treatment. Carburization of the iron by the illuminating gas in which it was heated is a possible explanation of the increase in resistivity. However, the resistance of the Kahlbaum iron was similarly affected by heating in nitrogen, the resistivity at 25°C. being increased from 10.527 microhm-cm. to 10.995 by heating to 1100°C. and cooling; a second heating increased the resistivity to 11.008 microhm-cm. On the other hand, Ribbeck[684] found no such increase for iron heated in nitrogen. Regardless of the

* International Critical Tables, vol. 6, p. 136.

TABLE 29.—THE ELECTRIC RESISTIVITY OF IRON AT ELEVATED TEMPERATURES

Investigator	Year	Material	Resistivity, microhm-cm.														
			(32°F.) 0°C.	(210°F.) 100°C.	(390°F.) 200°C.	(570°F.) 300°C.	(750°F.) 400°C.	(930°F.) 500°C.	(1110°F.) 600°C.	(1290°F.) 700°C.	(1380°F.) 750°C.	(1470°F.) 800°C.	(1650°F.) 900°C.	(1740°F.) 950°C.	(1830°F.) 1000°C.	(1920°F.) 1050°C.	(2010°F.) 1100°C.
Morris[35]	1897	Transformer iron	10.1*	16.5	24.3	34.6	45.0	57.2	71.5	87.8	96.5	106.8	115.2	117.8	118.8	119.9	121.0
Nicolai[187]	1908	Kahlbaum iron	10.68	16.63	23.93	32.78	43.45										
Meyer[246]	1911	Kahlbaum iron	8.53	15.53	25.00	35.41	46.80	59.85	76.35	96.65	104.8	107.8	111.1	112.8	113.6		
Meyer[246]	1911	Basic open-hearth ingot iron	9.57	15.39	23.69	34.18	47.80	62.35	79.55	103.3	113.2	118.6	121.2	122.0	122.4		
Meyer[246]	1911	Electrolytic iron	9.35	15.49	27.76	31.93	43.20	56.70	71.05	92.9	105.1	111.0	117.8	118.9	119.9		121.0
Honda and Ogura[344]	1914	Kahlbaum iron	16.5*	23.0	29.0	39.5	49.0	61.5	77.0	95.0	96.8	106.5	115.2	117.8	118.9	119.9	121.0
Burgess and Kellberg[324]	1915	Electrolytic iron	8.8	14.4	21.7	30.8	41.7	54.5	69.6	86.8	96.9	105.5	111.1† / 110.6‡	112.4			
Saldau[383]	1916	Kahlbaum iron (heating)	9.2*	15.08	20.98	29.50	41.24	54.74	70.23	87.15	96.51	106.6	117.0	121.4	122.7	124.1	125.4
Saldau[383]	1916	Kahlbaum iron (cooling)	9.3*	15.85	24.31	32.77	41.12	57.62	72.03	90.03	102.3	111.7	119.7	121.5	122.8	124.4	
Saldau[383]	1916	Electrolytic iron (heating)	9.6*	15.47	24.53	32.53	44.30	57.84	72.55	89.82	103.7	109.8	116.7	118.6	120.4	122.2	123.6
Saldau[383]	1916	Electrolytic iron (cooling)	10.08*	16.21	26.85	36.49	47.11	60.89	75.78	97.38	108.4	113.4	118.4	119.8	121.1	122.4	
Honda and Simidu[332]	1917	Swedish iron	13.2	20.1	27.4	36.0	46.2	58.3	72.0	90.2	100.5	109.9	117.0				
Ribbeck[384]	1926	Electrolytic iron	8.9	14.6	22.2	31.0	40.9	53.6	68.1	85.5	96.0	105.6	113.6	115.3			
Powell[389]	1934	Basic open-hearth ingot iron	9.6	15.0	22.6	31.4	43.1	55.3	69.8	87.0		105.5			116.6		

* Extrapolated.
† Heating.
‡ Cooling.

original purity of the iron the pick-up of impurities indicated by Saldau's data precludes their acceptance as those of high-purity iron.

The investigation of Honda and Simidu[372] was undertaken primarily to determine the relation between thermal and electric conductivity, both being determined between 30 and 900°C. (85 and 1650°F.) on the same specimen of a Swedish charcoal iron of unstated composition. The resistivity values below 400°C. (750°F.) were higher than those reported by any other investigator except Honda and Ogura, owing possibly to the fact that the thermal-conductivity measurements required a specimen of dimensions scarcely suitable for precise determinations of electric resistivity.

In connection with an investigation of the resistivity of nickel steels, Ribbeck[684] determined the resistivity of electrolytic iron up to 1000°C. The iron was stated to contain 0.07 per cent manganese, 0.014 per cent phosphorus, less than 0.01 per cent carbon, and only traces of silicon, copper, sulphur, and chromium. The resistivity at 20°C. was 10.1 microhm-cm., the fundamental coefficient was 0.0064 per degree centigrade. By extrapolation the value 8.9 microhm-cm. was obtained for the resistivity at 0°C. Correction for impurities by the formula of Gumlich gave 9.62 microhm-cm. as the resistivity of pure iron at 20°C. Ribbeck's description of his technique does not indicate extreme precision; his temperature intervals were large, averaging 32° above 300°C.; an atmosphere of nitrogen which was used at high temperatures introduced a possibility of contamination of the specimen during the determination. Nevertheless his resistance-temperature curve coincides more nearly than does that of any other investigator with the Burgess and Kellberg curve which, in view of the precision of their work, is considered the most probable. The temperature-resistance curves diverge slightly above 800°C. (1470°F.), Ribbeck's curve showing a slightly greater increase in resistance with increasing temperature than does the Burgess-Kellberg curve. At 950°C. (1740°F.) Ribbeck's value for the resistivity of iron is 115.3 microhm-cm. as compared with the value 112.4, derived from the Burgess-Kellberg data.

Determinations of the resistivity of Armco iron between 0 and 800°C. (32 and 1470°F.) were reported recently by Powell.[1069]

His results, shown in Table 29, are in close agreement with the results obtained for electrolytic iron by other investigators.

There are no data available on the resistivity of high-purity iron between 1100°C. (2010°F.) and the melting point. Values for the resistivity of molten iron were reported by Bornemann and Wagenmann.[269] These were obtained by extrapolating to zero carbon content the resistivities of carbon steels. The temperature coefficient between 1505°C. (2740°F.) (their value for the melting point of iron) and 1650°C. (3000°F.) was 0.000366 per degree centigrade, based on the equation

$$\alpha = \frac{R_{1650} - R_{1505}}{R_{1505}(1650 - 1505)}$$

The data of Bornemann and Wagenmann were as follows:

Temperature, °C.	Resistivity, Microhm-cm.
1505	131
1550	133
1600	136
1650	138

97. Temperature Coefficient of Resistivity at Elevated Temperatures.—Values for the temperature coefficient of resistivity of a number of irons are given in Table 30. In many cases these values were computed from the reported data for resistivity, according to the customary equation,

$$\alpha = \frac{R_t - R_{t'}}{R_0(t - t')}$$

The temperature intervals in all of the investigations except that of Burgess and Kellberg were too great to fix closely the point of maximum slope of the temperature-resistance curve. The Burgess and Kellberg curve shows it to be at 757°C. (1395°F.) for their iron.

98. Summary of Resistivity at Elevated Temperatures.—Of the several investigations of the electric resistance versus temperature relation of iron, that of Burgess and Kellberg undoubtedly yielded the most precise results. This precision does not hold for the derived values of resistivity which are necessarily based on the approximate value for the resistivity at 20°C. of the Burgess-Kellberg iron and on the assumption that the resis-

TABLE 30.—TEMPERATURE COEFFICIENT OF RESISTIVITY OF IRON AT ELEVATED TEMPERATURES

Investigator	Year	Material	Temperature coefficient of resistivity × 100										
			0–100°C. (32–210°F.)	100–200°C. (210–390°F.)	200–300°C. (390–570°F.)	300–400°C. (570–750°F.)	400–500°C. (750–930°F.)	500–600°C. (930–1110°F.)	600–700°C. (1110–1290°F.)	700–800°C. (1290–1470°F.)	800–900°C. (1470–1650°F.)	900–1000°C. (1650–1830°F.)	1000–1100°C. (1830–2010°F.)
Morris[75]	1897	Transformer iron	0.63	0.77	1.02	1.03	1.21	1.41	1.61	1.88	0.83	0.36	0.21
Niccolai[182]	1908	Kahlbaum iron	0.56	0.68	0.83	1.00						0.46	0.53
Somerville[224]	1910	Soft iron	0.57	0.79	1.00	1.23	1.42	1.55	1.89	2.50	0.65	0.29	
Meyer[246]	1911	Kahlbaum iron	0.821	1.11	1.22	1.33	1.53	1.93	2.38	1.31	0.39	0.13	
Meyer[246]	1911	Basic open-hearth ingot iron	0.607	0.87	1.10	1.42	1.52	1.80	2.48	1.60	0.27		
Meyer[246]	1911	Electrolytic iron	0.657	0.78	0.98	1.20	1.44	1.53	2.34	1.93	0.73		
Burgess and Kellberg[326]	1915	Electrolytic iron	0.635	0.83	1.02	1.24	1.45	1.71	1.96	2.15	0.66	0.25	
Holborn[400]	1919	Electrolytic iron	0.66	0.83	1.02	1.81	1.41						
Ribbeck[684]	1926	Electrolytic iron	0.64	0.85	0.99	1.11	1.42	1.63	1.96	2.26	0.90	0.33	
Powell[1069]	1934	Basic open-hearth ingot iron	0.56	0.79	0.92	1.22	1.27	1.51	1.79	1.93			

tivities of the Burgess and Kellberg iron and the Wenner and Lindberg iron were the same. Although the precision of Ribbeck's work is open to question, the fact that his temperature-resistance curve conforms more closely to that of Burgess and Kellberg than do the others warrants acceptance of his data as
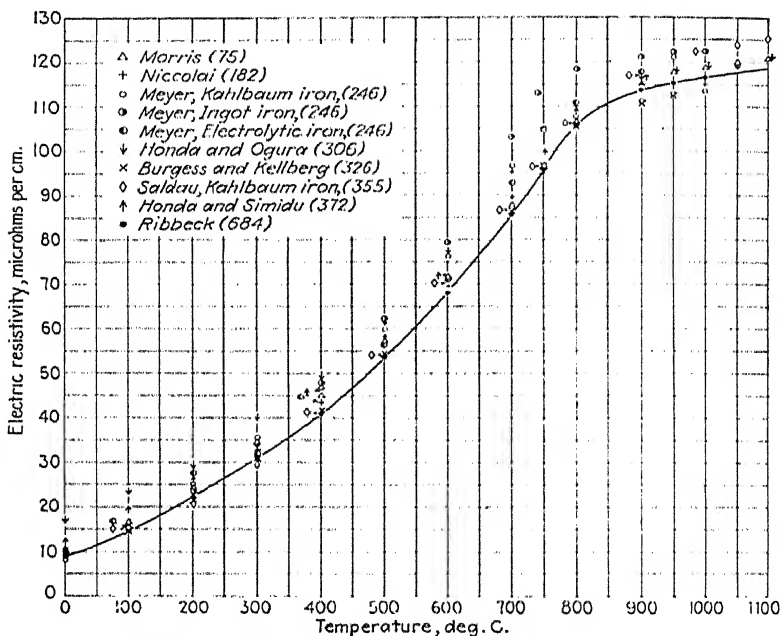
FIG. 24.—Electric resistivity of iron at elevated temperatures.

the most probable for the resistivity of iron above 100°C., with the reservation that resistivity-temperature data obtained on purer iron under conditions more suitable for retention of purity may differ somewhat from those of Ribbeck. Such resistivity data are not now available. A summary of the most probable values for the resistivity of iron at elevated temperatures is shown by the curve in Fig. 24.

99. Early Work on the Effect of Impurities.—The addition of another element increases the electric resistance of iron even though the element added has a lower resistance than iron. The

relation between the amount of impurity and the resulting increase in resistance has been the subject of many investigations, most of which have been concerned with the effect of foreign elements in amounts such as occur in carbon and alloy steels and not with the effects of the small amounts found in high-purity iron. In some of these investigations the results have been extrapolated to zero impurities to obtain values for resistivity of pure iron, consequently a review of the work on which these extrapolated values are based is included herewith, although an extended review of these investigations logically belongs in the monographs on the carbon and alloy steels.

The first quantitative measurements of the effects of impurities on the resistivity of iron seem to be those of LeChatelier,[80] in 1898, who observed that elements which form solid solutions exert a much greater effect than elements which are insoluble. Computed increases in resistivity for each per cent of impurity were: cementite, 7 microhm-cm.; silicon, 14 microhm-cm.; manganese, 5 microhm-cm. in magnetic steels and 35 microhm-cm. in non-magnetic steels. By extrapolation, the value 9.5 microhm-cm. was obtained for the resistivity of pure iron, presumably at room temperature. Results of resistance measurements on a large number of steels by Barrett, Brown, and Hadfield[100] indicated that the effect of the different elements was approximately proportional to the reciprocal of their atomic weights. Benedicks[107] expanded the idea, suggesting that equivalent quantities of foreign elements in iron caused equal increases in resistance and that the total increase in resistance caused by the impurities in any iron could be obtained from the total of these impurities expressed as equivalent quantities of one element whose effect per unit quantity was known. Measurements on a series of carbon steels indicated that the resistivity increased 26.8 microhm-cm. for one per cent increase in carbon content. By extrapolation Benedicks obtained the value 7.6 microhm-cm. for the resistivity of pure iron at 16°C. (61°F.), and proposed the use of a simple formula whereby the resistivity of any alloy of iron could be computed from the sum of the "carbon equivalents" of the elements present. However, all later work seems to indicate that the impurity-resistivity relationship in iron is not so simple as Benedicks' formula would indicate. Portevin[199,310] found that although the formula might be

accepted for small amounts of impurities, that is, for dilute solid solutions, it was not accurate for alloying elements in the amounts present in alloy steels. He also criticized Benedicks' assumptions regarding the form in which carbon was present in the steels with which Benedicks worked.

100. Recent Work on the Effect of Impurities.— Norbury[417] reviewed the work up to 1920 on the effect of foreign elements on the resistivity of iron and selected the values which he considered most probable. These are given in Table 31. From these data Norbury concluded that Benedicks' formula could not be considered correct. McCance, in discussion of Norbury's paper, also criticized Benedicks' formula and stated that the effect of an element on resistivity depends on the state of combination of the added element. In the case of carbide-forming elements, such as vanadium, chromium, and tungsten, the effect of the element would depend on the carbon content.

TABLE 31.—EFFECT OF FOREIGN ELEMENTS ON THE RESISTIVITY OF IRON*

Element	Increase in resistivity of iron, microhm-cm.	
	Per 1 weight per cent of added element	Per 1 atomic per cent of added element
Carbon......	34.0	7.3
Nitrogen.....	14.6	3.6
Aluminum...	12.0	5.8
Silicon........	13.5	6.9
Phosphorus..	11.0	6.1
Vanadium....	5.0	4.6
Chromium...	5.4	5.0
Manganese...	5.0	4.9
Nickel.......	1.5	1.5
Cobalt.......	1.0	1.0
Copper......	4.0	4.5
Molybdenum.	3.4	5.8
Tungsten....	1.5	4.9
Gold........	1.1	3.9

* Norbury.[417]

Of the numerous investigations on the effect of impurities on the electric resistivity that of Yensen[590] in 1924 is outstanding.

Other investigators used commercial steels containing impurities in amounts usual in such materials, but Yensen's results were obtained on high-purity binary alloys prepared by additions of the alloying elements to electrolytic iron. Yensen also noted the effect on the resistivity of small additions of the alloying element as well as of the larger amounts contained in commercial steels. His results on resistivity are given in Table 32.

TABLE 32.—EFFECT OF ADDED ELEMENTS ON THE RESISTIVITY OF IRON[*]

Element	Increase in Resistivity, Microhm-cm., per 1 Per Cent of Added Impurity
Carbon:	
Up to 0.02 per cent	82.5
0.02 to 0.85 per cent	4.5
Phosphorus:	
Up to 0.015 per cent	60.0
0.015 to 0.12 per cent	3.5
Silicon:	
Up to 0.35 per cent	18.4
0.35 to 6.0 per cent	11.1
Sulphur	12.0
Manganese	7.0

[*] Yensen.[590]

Calculating the resistivity of pure iron from his values for electrolytic iron by the formula

$$R_0 = R - 82.5C - 7.0Mn - 60P - 18.4Si - 12S$$

where R_0 is the resistivity of pure iron, R the resistivity of electrolytic iron, and C, Mn, etc., the percentage of each element present, Yensen obtained the value 9.6 microhm-cm. at 20°C.

Application of Yensen's formula to the value 9.78 microhm-cm. at 20°C., obtained by Wenner and Lindberg[834] on an electrolytic iron, said to contain 0.003 per cent carbon, 0.004 per cent phosphorus, 0.004 per cent silicon, 0.006 per cent sulphur, and a trace of manganese, gives 9.18 microhm-cm. for the electric resistance of pure iron at 20°C., a much lower value than that obtained by Yensen.

101. Summary of the Effect of Impurities.—Although values for the effect of impurities may be of some use in calculating approximate resistivities of commercial irons and steels, they

are of dubious worth as a means of obtaining values for pure iron. These values for the effect of impurities are averages for the effect over a considerable range of impurity, and there is no assurance that the effect is uniform over the range, in fact Yensen found that a quantity of carbon under 0.02 per cent had 18 times as much effect on the resistivity as did the same quantity above 0.02 per cent. Similar results applied to phosphorus contents under and over 0.015 per cent. Furthermore, it is unsafe to assume that the effects of several impurities are additive, *i.e.*, that the effect of a specific impurity will not be influenced by the presence of other impurities. Reported values for the electric resistance of pure iron, obtained by extrapolation of results from impure materials, range from 7.6 to 10.12 microhm-cm., an indication of the unreliability of the method.

102. Influence of Mechanical and Thermal Treatment.— Investigations of the effect of mechanical and thermal treatment on the resistivity of high-purity iron are few, the bulk of the work being on the less pure forms of iron. As would be expected, the electric resistivity of iron increases with cold work but is restored to the original value by annealing at a suitable temperature.

No relation between amount of cold work and change in resistivity (or conductivity) is apparent in the results of Bardenheuer and Schmidt,[764] given in Table 33, on cold-drawn electrolytic iron stated to contain 0.03 per cent of impurities. The

TABLE 33.—EFFECT OF COLD WORK ON THE RESISTIVITY OF ELECTROLYTIC IRON*

Reduction in area, per cent	Conductivity, mho per sq. mm. per m.	Resistivity, microhm-cm.
0	9.33	10.72
20	9.35	10.69
30	8.94	11.18
50	8.99	11.12
60	9.25	10.81
75	9.03	11.07
95	9.23	10.83

* Bardenheuer and Schmidt.[764]

annealing temperature giving the maximum restoration of conductivity was 500°C. (930°F.) regardless of the degree of cold work. Experiments with an ingot iron indicated that the conductivity of iron is independent of grain size.

Tammann and Moritz[1031] obtained a maximum increase in resistivity of about 5.7 per cent by cold working to 0.2 per cent of the original area of cross section (99.8 per cent reduction). As indicated in Fig. 25, the annealing temperature for maximum recovery, about 600°C. (1110°F.), was independent of the degree of cold work. The resistivity of iron wire, cold worked to 98.7 per cent reduction, was restored to its original value by annealing at 520°C. (970°F.) for about 75 min. Annealing at lower temperatures caused the resistivity to decrease suddenly to values which remained almost constant but which did not decrease to the original value regardless of the length of anneal up to 2 hr., as shown in Fig. 26. The temperature coefficient was decreased by cold working and was restored by the same annealing conditions which restored the resistivity.

FIG. 25.—Effect of annealing on the electric resistance of cold-worked iron. Reduction in area of 97.8 per cent obtained by rolling; other reductions obtained by cold drawing. (*Tammann and Moritz*.[1031])

The effect of pressure on the conductivity of iron was investigated by Beckman[325] and by Bridgman.[347] The former used a Swedish iron of low purity, judging by its fundamental coefficient of 0.0048. The value for the pressure coefficient ($a = 1/R \times dR/dP$) of this material was 27.4×10^{-7} per atmosphere between 425 and 2097 atmospheres at 0°C. Bridgman used a basic open-hearth iron with a fundamental coefficient of 0.0062 and obtained values for the pressure coefficient at 0°C. of

24.9×10^{-7} per atmosphere at zero pressure and 21.9×10^{-7} per atmosphere at 12,400 atmospheres.

B. THERMAL ELECTROMOTIVE FORCE

If iron is connected in series with another metal M so that a closed circuit is formed, and if the two junctions are at different temperatures, an electric current will flow through the circuit. If one junction is kept at 0°C. and the other at temperature t,
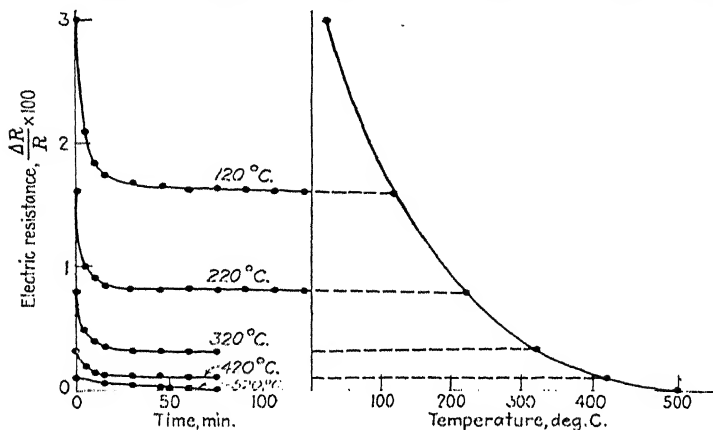
FIG. 26.—Relation between annealing time and electric resistance of cold-drawn electrolytic iron. Reduction in area 98.7 per cent. (*Tammann and Moritz*.[1031])

the value of the electromotive force $_{Fe}E_M$, for a limited range of temperature may be expressed by an equation of the form:

$$_{Fe}E_M = at + \tfrac{1}{2}bt^2 + \tfrac{1}{3}ct^3$$

where a, b, and c are numerical constants for a particular pair of metals. The thermal electromotive force is conveniently expressed in millivolts and is considered positive if the current flows from iron to the other metal at the junction which is at 0°C.

The thermoelectric power, at any temperature t, is the thermal electromotive force per degree of temperature difference between the two junctions and may be expressed, for a limited range of temperature, by an equation of the form

$$\frac{dE}{dt} = a + bt + ct^2$$

where *a*, *b*, and *c* are the same numerical constants that were used in the equation for the thermal electromotive force. The thermoelectric power is a smaller numerical value than the thermal electromotive force and is conveniently expressed in microvolts per degree.

The purity and previous history of the sample affect the results obtained in the determination of many of the properties of iron,
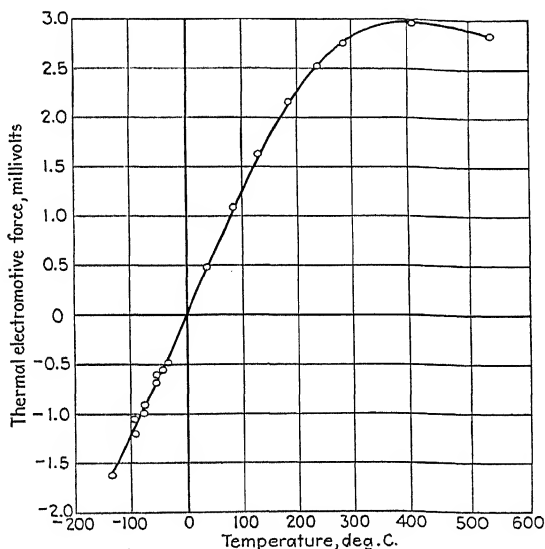
Fig. 27.—Thermal electromotive force of iron versus aluminum. (*Dannecker.*[277])

but in measurements of thermoelectric properties there are the additional factors of the purity and previous history of the second metal which, with iron, constitutes the thermocouple.

Many of the data found in the literature and presented in this section were obtained with metals of doubtful purity and, although presumably accurate for the particular specimens used, they would probably not be duplicated by measurements on high-purity metals.

The curves and data in this section, unless otherwise stated, are for thermocouples with the cold junction maintained at 0°C.

103. The Iron-aluminum Thermocouple.— Dannecker[277] determined the thermal electromotive force of the iron-aluminum couple. His data, reproduced in Fig. 27, indicated a neutral point at about 400°C. (750°F.).

104. The Iron-constantan Thermocouple.— The thermal electromotive force of iron against constantan* in the temperature range −183 to +100°C. (−295 to +210°F.) could be expressed according to Molby,[217] by the equation:

$$_{Fe}E_{constantan} = 52,677t + 0.0288t^2 - 0.0000132222t^3$$

Onnes and Crommelin[146] stated that a five-term equation was necessary to represent the electromotive force of the thermoelement steel-constantan between 0 and −217°C. (32 and −360°F.) and that a sixth term was necessary to include liquid-hydrogen temperature. Onnes and Clay[183A] found the iron-constantan thermocouple unsatisfactory for very low temperatures because of the slight increase in e.m.f. with decrease in temperature. Their results were:

Temperature, °C	−217.42	−252.93	−259.24
E.m.f., millivolts	6.83	7.13	7.16

Values for the thermal electromotive force of iron-constantan at elevated temperatures have been given by a number of investigators including Bausenwein,[118] Hoffmann and Schulze,[414] Schwartz,[266] and Dannecker.[277] Specimens of constantan from different sources vary considerably in composition and in

* Constantan is the general name of a type of alloys which consist essentially of copper and nickel with manganese, carbon, iron, and perhaps other elements present as minor constituents. Other names such as Advance, Copel, Copnic, and Ideal have been applied to alloys of this type but, in the United States, the term *constantan* is generally used at present.

International Critical Tables[670A] gives the following range of composition for constantan alloys:

Element	Percentage
Copper	60 to 45
Nickel	40 to 55
Manganese	0 to 1.4
Carbon	0.1
Iron	Present
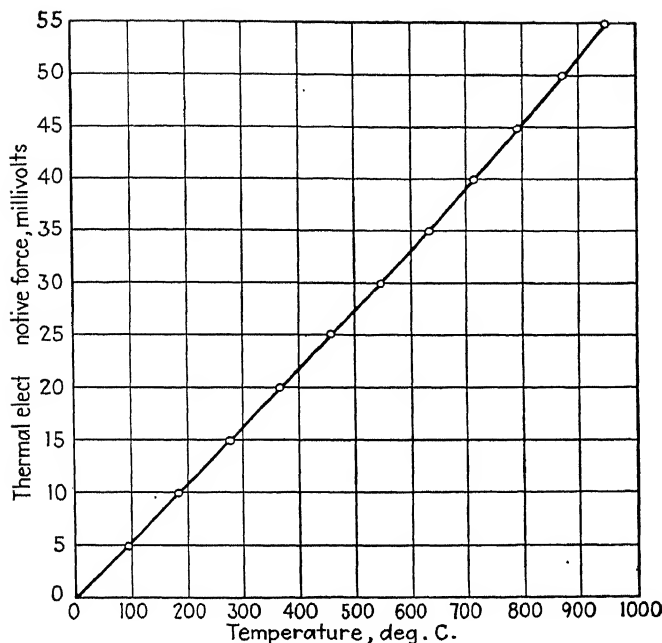
Fig. 28.—Thermal electromotive force of iron versus constantan. (*International Critical Tables.*[6704])

TABLE 34.—THERMAL ELECTROMOTIVE FORCE OF THE IRON-CONSTANTAN THERMOCOUPLE*

Temperature		E.m.f., millivolts	Temperature		E.m.f., millivolts
°C.	°F.		°C.	°F.	
0	32	0	546	1015	30
95	203	5	632	1170	35
186	367	10	713	1315	40
277	530	15	792	1458	45
367	693	20	871	1600	50
457	855	25	950	1742	55

* International Critical Tables.[6704]

thermoelectric power; therefore, the values for iron against constantan given by different investigators vary considerably. The values in Table 34 and Fig. 28 from the International Critical Tables[670.4] illustrate results which have been obtained for this type of couple.

The combination of iron with constantan is the only thermocouple, with iron as one element, which has found appreciable use. The relatively large potential developed by this couple makes it a useful instrument for temperatures below 950 or 1000°C. (1740 or 1830°F.).

105. The Iron-copper Thermocouple. Harrison[110] reported the following values for the thermal electromotive force of the iron-copper couple:

Temperature, °C..........	−191.2	+11.2	99.9	182.5	445.5
E.m.f., millivolts........	− 2.19	+ 0.1	+0.87	+1.33	+0.68

Harrison found that his results could be approximately expressed by the equation:

$$E_0^t \text{ (microvolts)} = 11.228t + 0.021924t^2$$

The data of Bausenwein[118] for iron-copper, based on 20°C. (68°F.) for the cold junction instead of 0°C. as is customary, are given in Table 35.

TABLE 35.— THERMAL ELECTROMOTIVE FORCE OF THE IRON-COPPER THERMOCOUPLE, COLD JUNCTION AT 20°C.*

Temperature		E.m.f., millivolts	Temperature		E.m.f., millivolts
°C.	°F.		°C.	°F.	
20	68	0.0	460	860	+0.9
60	140	+0.3	510	950	+0.5
110	230	0.6	560	1040	+0.1
160	320	0.8	610	1130	−0.4
210	410	1.1	660	1220	−0.8
260	500	1.2	710	1310	−1.4
310	590	1.3	760	1400	−1.7
360	680	1.2	810	1490	−2.1
410	770	1.1			

* Bausenwein.[118]

The transformation temperatures shown on Broniewski's[272] curve for the thermal electromotive force of iron-copper indicated that his temperature measurements were erroneous. Values reported by Onnes and Holst[309] for the thermal electromotive force of iron against copper at low temperatures (reference junction at $+16°C.$) were:

Temperature, °C............	−192.2	−253.2	−268.9	−270.0
E.m.f., millivolts..........	− 1.29	− 1.32	− 1.31	− 1.31

The data of Dannecker[277] for the iron-copper thermocouple (Fig. 29) place the neutral point at 247°C (475°F.) and the inversion point at 527.5°C. (981.5°F.).
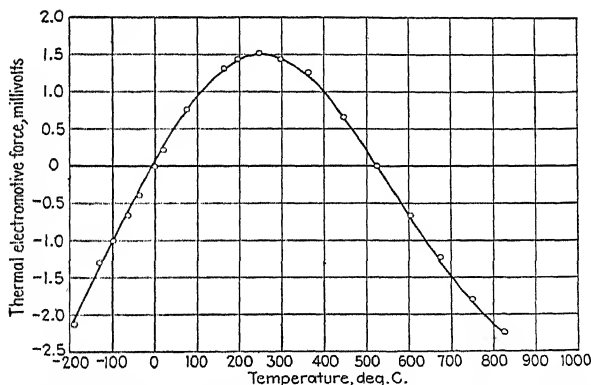
Fig. 29.—Thermal electromotive force of iron versus copper. (*Dannecker.*[277])

106. The Iron-lead Thermocouple.—The thermal electromotive force of iron against lead at low temperatures was determined by Dewar and Fleming[65] for annealed transformer iron and by Wietzel[320] for Heraeus electrolytic iron, according to the data in Fig. 30. Dewar and Fleming also reported the value 14.5 millivolts as the thermal electromotive force of iron-lead at 100°C. Bridgman[364] studied the iron-lead couple at temperatures between 0 and 100°C. and computed values for the constants a, b, and c, in the general equation, for this range of temperature.

Bridgman's determination of 14.4 millivolts for the thermal electromotive force of iron-lead at 100°C. is in excellent agreement with the similar determination of Dewar and Fleming.
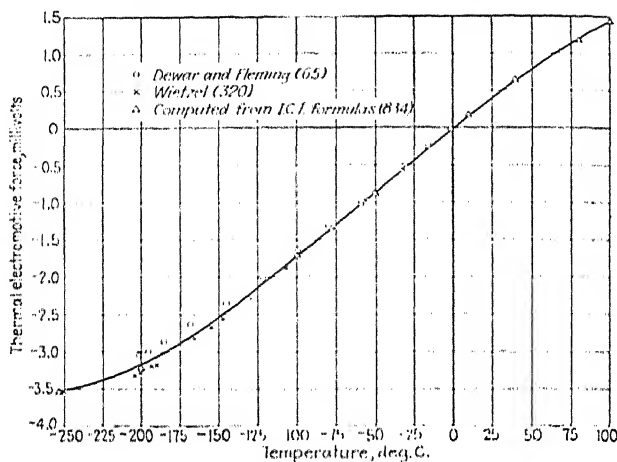
FIG. 30.   Thermal electromotive force of iron versus lead.

107. The Iron-nickel and Iron-platinum Thermocouples. Harrison[110] gave the following values for the thermal electromotive force of iron-nickel:

Temperature, °C.	—191.2	+100	200	500
E.m.f., millivolts	— 5.11	+ 3.13	6.16	11.81

The more complete data of Dannecker[277] are reproduced in Fig. 31.

In view of the probable impurity of metals and deficiency of pyrometry in the early work on the iron-platinum thermocouple, the results of the early investigations can be omitted from consideration in favor of the two outstanding investigations on the subject, those of Burgess and Scott,[348] whose values have been selected for the International Critical Tables, and of Goetz,[561] whose values are reported in the Landolt-Börnstein Tables.   The values obtained in these investigations for the thermoelectric

power dE/dt of iron against platinum are shown in Fig. 32. The two curves at temperatures of about 900°C. (1650°F.) illustrate
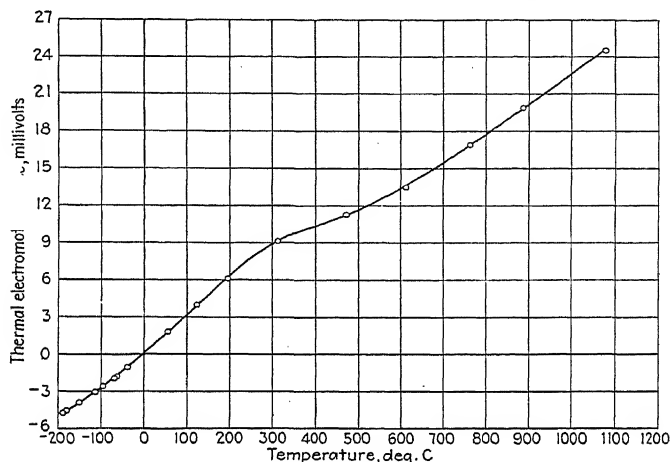
FIG. 31.—Thermal electromotive force of iron versus nickel. (*Dannecker.*[277])
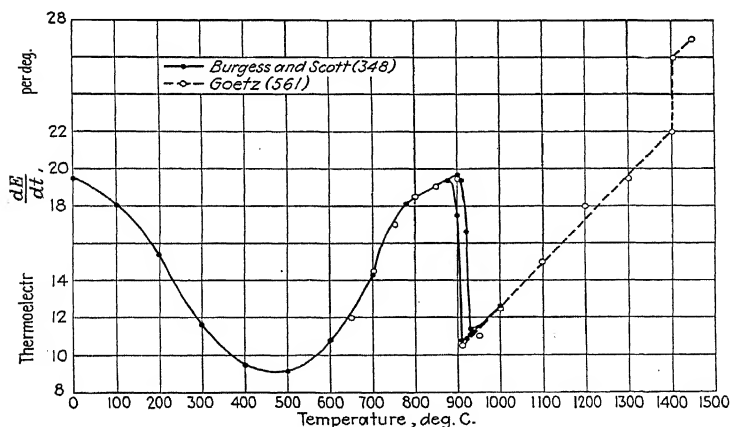
FIG. 32.—Thermoelectric power of iron versus platinum.

the observation of Burgess and Scott that higher values were obtained on heating in the A_3 range than were obtained on cooling through the same temperature range.

108. The Iron-tin Thermocouple.—The thermoelectric power dE/dt of the iron-tin couple was determined by Cermak and Schmidt.[231] Their results are given in Table 36.

TABLE 36.—THERMOELECTRIC POWER OF THE IRON-TIN THERMOCOUPLE*

Temperature		Thermoelectric power, micro- volts per °C.	Temperature		Thermoelectric power, micro- volts per °C.
°C.	°F.		°C.	°F.	
147	297	11.5	247	477	4.1
157	315	10.1	257	495	3.6
167	333	9.3	267	513	3.5
177	351	8.9	277	531	2.7
187	369	8.4	287	549	1.9
197	387	8.2	297	567	1.6
207	405	8.2	307	585	1.1
217	423	6.9	317	603	0.6
227	441	6.0	327	621	0.2
237	459	4.4			

* Cermak and Schmidt.[231]

The values of Smits and Spuyman[449] for the thermal electromotive force of the iron-tin couple are given in Fig. 33. They
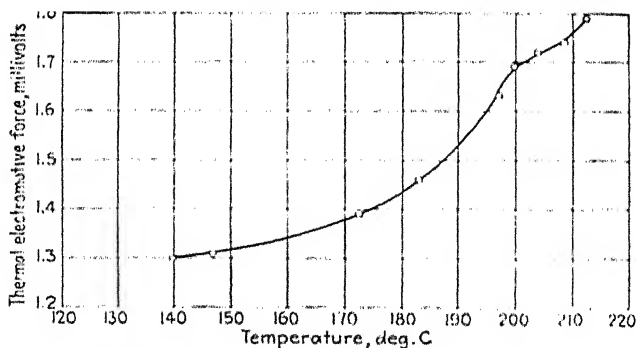
FIG. 33.—Thermal electromotive force of iron versus tin. (*Smits and Spuyman.*[449])

ascribed the change in slope of the curve at 200°C. (390°F.) to the transition of tin from the tetragonal to the rhombic form.

109. Influence of Impurities and Previous History.—The information available on the effect of impurities on the thermo-

electric properties of iron is rather meager. Broniewski[272] gave the following equations as representing the thermoelectric power of a series of iron-carbon alloy couples with copper, between 0 and 700°C. (32 and 1290°F.):

Material	Thermoelectric Power dE/dt
Electrolytic iron	$13.7 - 7.8t \times 10^{-2} + 6.6t^2 \times 10^{-5}$
Iron (0.07 per cent C)	$18.1 - 9.86t \times 10^{-2} + 9.0t^2 \times 10^{-5}$
Steel (0.24 per cent C)	$16.6 - 9.06t \times 10^{-2} + 8.1t^2 \times 10^{-5}$
Steel (0.44 per cent C)	$14.8 - 8.12t \times 10^{-2} + 7.2t^2 \times 10^{-5}$
Steel (0.79 per cent C)	$13.4 - 7.98t \times 10^{-2} + 6.9t^2 \times 10^{-5}$
Steel (1.12 per cent C)	$12.2 - 7.2t \times 10^{-2} + 6.3t^2 \times 10^{-5}$

Dupuy and Portevin[328] found that the thermal electromotive force of iron, against lead, was decreased 5.6 microvolts per degree between −80 and 0°C. (−110 and 32°F.) and 4.6 microvolts per degree between 0 and 100°C. for each per cent of carbon present, the data being obtained on a series of carbon steels. The effects of nickel, chromium, molybdenum, manganese, aluminum, silicon, and tungsten in alloy steels also were studied. Campbell[350] determined the thermal electromotive force at 100°C., with the cold junction at 0°C., of couples composed of heat-treated steel and annealed open-hearth iron. His results, given in Table 37, indicate the effect of carbon as well as of heat treatment. Campbell found that mechanical working affected the

TABLE 37.—INFLUENCE OF HEAT TREATMENT ON THERMAL ELECTROMOTIVE FORCE OF CARBON STEELS AGAINST OPEN-HEARTH IRON, AT 100°C. (212°F.)*

Carbon, per cent	Quenched from 905 to 908°C. (1661 to 1666°F.)	Thermal electromotive force, microvolts							
		Annealed at							
		100°C. (212°F.)	205°C. (401°F.)	309°C. (588°F.)	388°C. (730°F.)	495°C. (923°F.)	599°C. (1110°F.)	696°C. (1285°F.)	800°C. (1472°F.)
0.04	74	36	34	29	34	29	29	26	29
0.30	310	278	230	170	136	102	94	83	100
0.35	575	537	499	452	437	419	414	400	413
0.41	615	578	529	474	444	434	429	414	420
0.57	707	627	537	474	444	419	414	394	417
0.76	950	718	577	474	439	410	404	350	393
0.945	1170	795	608	458	410	392	376	364	378
1.05	1308	916	713	556	516	509	497	467	473

* Campbell.[350]

thermal electromotive force of iron only slightly, results at 0 and 100°C. differing by only 10 microvolts for a thermocouple composed of annealed basic open-hearth iron and the same material cold-worked sufficiently to increase the Brinell hardness from 76 to 240. Limited data accumulated at the National Bureau of Standards indicate that cold working may change the thermal e.m.f. considerably more than 10 microvolts, the change in isolated instances being about ten times that noted by Campbell. In a recent paper by Tammann and Bandel[1030] it was reported that 98 per cent reduction by cold drawing decreased the thermoelectric power of electrolytic iron by 0.43 microvolt per °C. The thermoelectric power of this strained iron was affected by annealing at temperatures as low as 70°C. (160°F.) and was restored to its original value by annealing at 320°C. (610°F.). Tammann and Bandel also found that torsion (twisting the wire 6 revolutions for each centimeter of length) decreased the thermoelectric power of electrolytic iron. The change which resulted from this amount of torsion was about one-third as great as the change produced by 98 per cent reduction in cold drawing.

The influence of pressure and of tension on the thermoelectric power of iron was investigated by Bridgman.[364] The variations of the electromotive force with pressure were complicated, there being maxima and minima with both pressure and temperature within the range 0 to 100°C. The effects of tension at two temperatures were expressed by the formulas:

$$\text{At } 52°\text{C., e.m.f.} = (0.0120T - 0.04235T^2) \times 10^{-6} \text{ volt}$$
$$\text{At } 95°\text{C., e.m.f.} = (0.0223T - 0.0442T^2) \times 10^{-6} \text{ volt}$$

where T is the tension in kilograms per square centimeter acting on one component of the thermocouple, the other being unstressed.

C. PELTIER EFFECT

If a current is passed through a junction of iron and another metal M in the same direction that a current would pass if the junction were heated, heat is absorbed and the junction is thereby cooled. The phenomenon is reversible; if the current is passed through the junction in the opposite direction, an equal amount of heat is evolved and the junction is thereby heated. The amount of heat absorbed per ampere of current is the

Peltier coefficient of iron against the metal M. This coefficient theoretically can be computed from the thermoelectric power by means of the equation

$$_{\text{Fe}}P_M = T\frac{dE}{dt}$$

where $_{\text{Fe}}P_M$ is the Peltier coefficient; T is the absolute temperature; and dE/dt is the thermoelectric power.

The Peltier effect of iron against platinum, according to Burgess and Scott[348] and as calculated from the data of Goetz,[561] is given in Table 38. Burgess and Scott used small enough tem-

TABLE 38.—PELTIER EFFECT OF IRON AGAINST PLATINUM

Temperature, °C.	Peltier coefficient, microvolts		Temperature, °C.	Peltier coefficient, microvolts		
	Burgess and Scott[348]	Goetz[561]		Burgess and Scott[348]		Goetz[561]
0	5,320	......	880	22,350		
100	6,750	......	900	23,100*	20,510†	22,870
200	7,280	......	910	22,940	12,770	12,420
300	6,700	......	920	19,800	13,000	
400	6,390	......	930	13,710	13,350	
500	7,030	......	950	....	....	13,450
600	9,430	......	1000	16,040‡		15,910
650	......	11,080	1100	....		20,600
700	13,910	14,110	1200	....		26,520
750	......	17,390	1300	....		30,670
780	18,980	......	1400	....		38,480
800	19,740	19,850	1405	....		43,630
850	......	21,340	1450	....		46,920

* Heating.
† Cooling.
‡ Corrected.

perature intervals, in the vicinity of the A_3 transformation, to show that hysteresis occurs in the thermoelectric properties in that temperature range. Cermak[154] reported that the Peltier coefficient in iron-constantan increased with increasing temperature, from 3.1×10^{-3} cal. per coulomb at 0°C. to 12.5×10^{-3} at 560°C.

The values for the Peltier coefficient of iron against other metals as reported in International Critical Tables[834] are reproduced in Table 39.

TABLE 39.—PELTIER COEFFICIENT OF IRON*

Metals	Temperature, °C.	Peltier coefficient, microvolts	Investigator
Iron-copper..	0	+3680	Jahn[42]
Iron-copper...	19	+2893	Gottstein[303]
Iron-copper...	20	+2995	Borelius[363]
Iron-copper...	25	+2930	Le Roux[15]
Iron-mercury.	18.5	+4880	Oosterhuis[263]
Iron-nickel...	15	+9600	Beck[206]

* International Critical Tables.[834]

The influence of pressure on the Peltier effect at temperatures between 0 and 100°C. was investigated by Bridgman.[364] The Peltier coefficient for iron against lead was negative at 0°C. with all pressures; with increasing temperature it became positive, increased to a positive maximum and then decreased. According to Bridgman, the Peltier coefficient for iron against lead can be expressed in the temperature range 0 to 100°C. by the equation:

$$_{Fe}P_{Pb} = (16.18 - 0.0178t - 0.000258t^2)(t + 273)(10^{-6}) \text{ volt}$$

D. THOMSON EFFECT

If an electric current is passed through a specimen of iron in which a temperature gradient exists, heat is absorbed if the current flows from the regions of higher temperature to those of lower temperature. Conversely, heat is evolved if the electric current flows in the opposite direction, *i.e.*, from regions of low temperature to those of higher temperature. This evolution or absorption of heat is known as the Thomson effect. It has been expressed in various units by different investigators and there has been disagreement as to the algebraic sign of the coefficient. The compilers of the International Critical Tables[834] converted the various units in which different investigators reported their results to microvolts per degree centigrade and adopted the convention that the sign of the coefficient is positive when absorption of heat accompanies the passage of current in the direction from

higher to lower temperatures. This reference[834] also gives an equation for expressing the Thomson coefficient δ in microvolts per degree centigrade as follows:

$$\delta = \alpha + \beta t \times 10^{-2} + \gamma t^2 \times 10^{-5}$$

where t is the temperature at which the determination is made, and α, β, and γ are constants for the particular metal and for a limited range of temperature. The values reported[834] for these constants and the temperature ranges within which these values apply, together with values reported by Bridgman,[364] are reproduced in Table 40.

TABLE 40.—CONSTANTS FOR THE COMPUTATION OF THE THOMSON
COEFFICIENT FOR IRON

Temperature range, °C.				Investigator
−51 to +115	+ 4.00	+ 8.4		Berg[207]
+32 to +182	+ 7.66	+ 4.1	+17	Hall et al.[144]
+53 to +308	+ 2.97	+ 1.85		Battelli[35]
at 48°	+11.3			Koenigsberger and Weiss[245]
+49 to +148	−16.4	+20.8		Aalderink[203]
+91 to +441	+ 7.785	+ 8.61	−21.4	Lecher[145]
0 to 100	+ 4.86	+15.87	5.16	Bridgman[364]

The effect of pressure on the Thomson effect as reported by Bridgman[364] is complicated; at higher pressures, there are two reversals between 0 and 100°C. Young[591] determined the Thomson effect in basic open-hearth ingot iron and in three carbon steels. The values obtained depended on whether the electric current flowed with or against the temperature gradient, owing, he concluded, to asymmetry. The effect of increasing carbon content was to decrease the value of the Thomson coefficient.

E. AUTHORS' SUMMARY

The resistivity of iron is affected by the presence of impurities, and is particularly affected by the presence of the first traces of some of the common impurities. It has been shown that the effect is very pronounced for carbon contents of less than 0.02 per

cent or for phosphorus contents of less than 0.015 per cent. The resistivity also is affected by the physical condition of the material and perhaps by other factors. However, even with due allowance for these variables, available data for the different determinations of the resistivity of high-purity iron are not in good agreement.

Available data for the resistivity at temperatures between −273 and +1100°C. (−460 and +2010°F.) are shown in Figs. 23 and 24 (pp. 175 and 188) with the selected values indicated by solid lines. There are practically no data for the resistivity of high-purity iron at any temperature above 1100°C. It is suggested that 9.8 microhm-cm., for the resistivity at 20°C., and 0.0065, for the fundamental coefficient (the temperature coefficient of resistance for the range from 0 to 100°C.), be accepted as the best present approximations for these properties of high-purity iron.

The thermoelectric power of iron against platinum (the standard reference material in thermoelectric measurements) was determined by Burgess and Scott[348] for the temperature range from 0 to 1000°C. (32 to 1830°F.) and by Goetz[561] for the range from 650 to 1450°C. (1200 to 2640°F.). Within the range from 650 to 1000°C. the two sets of data are in excellent agreement. Determinations of thermal e.m.f. against a reference metal such as pure platinum may be of value in comparing the purity of different samples of high-purity iron but further data are needed for the quantitative interpretation of such measurements.

The data for iron versus platinum are the only thermoelectric data which can be accepted as relatively accurate for high-purity metals. The thermoelectric properties are appreciably affected by the purity and physical condition of both of the metals of the thermocouples. Figures 27 to 33 (pp. 195 to 202) show the effect of temperature on the properties of thermocouples of iron with another metal, but the data in general can be accepted as applicable in a quantitative manner only to the particular thermocouple that was used, not to the properties of pure metals nor to the properties of other thermocouples of the same combinations of metals.

The thermocouple which consists of iron and constantan is the only thermocouple of iron which has found appreciable use. Constantan is the name of a type of alloy rather than of a certain rigidly defined composition; consequently there are several con-

stantans each with its own e.m.f. against iron. The relatively large potentials developed by this combination and the approximately constant slope of the curve between 0 and 1000°C. make it useful within this temperature range.

Other thermoelectric effects, such as the Peltier and Thomson effects, are matters of scientific or theoretical interest.

CHAPTER VII

MAGNETIC PROPERTIES

Magnetic Characteristics at Room Temperature— Effect of Temperature—Effect of Impurities—Effect of Grain Size— Effect of Cold Work and Heat Treatment—Mechanomagnetic Effects- Galvanomagnetic and Thermomagnetic Effects— Magnetic Properties of Single Crystals of Iron—Authors' Summary

The magnetism of iron is of considerable economic importance for it is largely by the magnetization of iron that the commercial conversion of mechanical to electric power, or of electric to mechanical power, is effected. On account of the importance of ferromagnetism its literature is voluminous, but the bulk of this literature is concerned more with the theory and mechanism of magnetism than with the magnetic properties of iron. Only that portion concerned with the latter will be considered here, as discussion of the theoretical aspects of ferromagnetism is beyond the scope of this monograph.

The magnetic properties of iron are so drastically affected by the presence of impurities, by the size and shape of the specimens, and by the previous mechanical and thermal treatment, that the magnetic data obtained on a specimen of iron represent the characteristics solely of that particular specimen and will be duplicated in other specimens only by coincidence. They do, however, indicate the approximate characteristics to be expected of iron of similar composition and history, but to be of real worth the composition and history of the iron must be completely specified. Unfortunately, satisfactory descriptions of the materials used in magnetic investigations have been the exception rather than the rule. Specimens have been classed as "annealed" without describing the annealing process or as "unannealed" without specifying the previous mechanical treatment. Analyses have rarely been reported, in many cases even the commercial designation of the irons has not been recorded as a clue to their composition. This situation necessitated disregarding limita-

tions on impurities in the selection of data on some of the magnetic effects. Such data are more of qualitative than quantitative worth; they indicate the direction but not necessarily the extent of the effects to be expected in iron of high purity.

110. Magnetic Terms and Definitions.—The magnetic properties of the ferromagnetic materials are commonly expressed
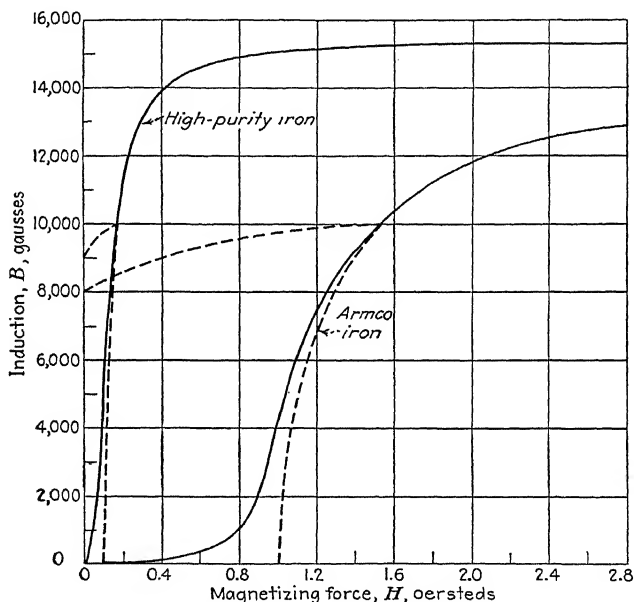
Fig. 34.—Magnetization curves for high-purity iron and Armco iron. (*Yensen.*[(989)])

in terms of corresponding values of the magnetic induction B and the magnetizing force or field strength H. In some cases quantities derived from B are used instead of B, for example the intrinsic induction $B - H$ or the intensity of magnetization I. Magnetic properties are conveniently expressed in the form of graphs obtained by plotting B, or some of the quantities derived from B, against H. The resulting curves are of two types, the curve of normal induction of which Fig. 34 is an illustration, and the hysteresis loop similar to Fig. 35.

Values for permeability (μ), susceptibility (K), and saturation intensity or intensity of magnetization at saturation (I_∞) can be derived from data for the normal induction curve, and values for hysteresis loss (W), residual induction (B_r), and coercive force (H_c) can be derived from data for the hysteresis loop.
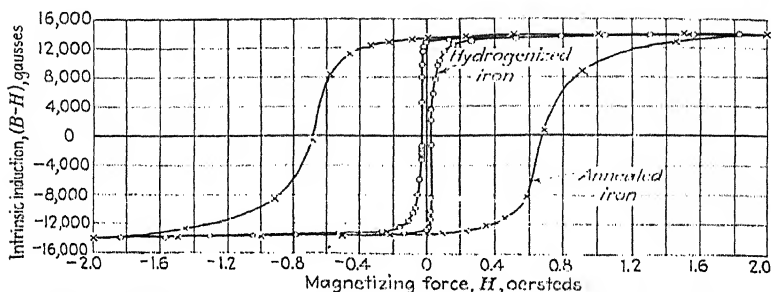
Fig. 35. — Hysteresis loops of annealed and of hydrogenized Armco iron.
(Cioffi.[964])

Some of the principal terms, symbols, and in some cases the units used in describing magnetic properties are as follows:

Magnetic induction = B (gausses)
Residual induction = B_r (gausses)
Magnetizing force or field strength = H (oersteds)
Coercive force = H_c (oersteds)
Intrinsic induction = $B - H$

Intensity of magnetization = $I = \dfrac{B - H}{4\pi}$

Permeability = μ $\dfrac{B}{H}$

Susceptibility* = $K = \dfrac{\imath}{H}$

Saturation intensity = I_∞
Hysteresis loss = W (ergs per cu. cm. per cycle)

The residual induction B_r is the induction remaining when the field is reduced to zero from $H_{\mathrm{max.}}$, the maximum field strength

* Susceptibilities of appreciable magnitude are usually expressed in terms of the volume susceptibility according to the above equation. However, in cases of weakly magnetic materials, such as paramagnetic iron, the susceptibility is sometimes expressed as mass susceptibility. The two terms differ by a factor equal to the density of iron. Unless otherwise stated, susceptibility is used in this monograph to mean volume susceptibility.

used in that experiment. The coercive force H_c is the value of the reverse magnetizing force necessary to reduce the induction to zero. The hysteresis loss W is proportional to the area of the hysteresis loop and represents the energy lost in carrying a cubic centimeter of the material through a complete magnetic cycle. The hysteresis loss is a function of the induction and can be expressed approximately by Steinmetz' formula which for iron is

$$W = \eta B^{1.6}$$

Values of the Steinmetz coefficient η are frequently mentioned in describing the magnetic properties of materials.

A. MAGNETIC CHARACTERISTICS AT ROOM TEMPERATURE

Probably the earliest investigation of the magnetic properties of annealed electrolytic iron was that of Gumlich[194,195] in 1909. The materials previously investigated were either electrolytic iron as deposited or commercial iron. The magnetic properties of the former were reported by Beetz[12] as early as 1860, by Holz[28] in 1874, and by others in the succeeding years. The properties of unannealed electrolytic iron differ greatly from those of annealed material. The differences are due, at least in part, to occluded hydrogen or to the distortion of the iron lattice which results from the occlusion of hydrogen. They will be considered in the discussion of the effect of hydrogen on the magnetic properties of iron.

The importance of the work of Rowland[27] in 1873 lies largely in the fact that he pioneered both in the use of absolute units in reporting his results and in developing the permeability-magnetization curves. For a specimen of Norway iron, one of the several materials investigated, he obtained a permeability of 5515, an unusually high value for that time.

The developments in the next three decades were in the line of improvement in the technique of magnetic measurements rather than in the quality of material. A sample of "unusually pure" commercial iron, stated to contain 0.013 per cent sulphur, 0.1 per cent manganese, and traces of carbon and silicon as impurities, had a permeability of 3344 for $B = 7060$ as reported by Lydall and Pocklington[55] in 1892. Wilson[34] in 1898 investigated the magnetic properties of the same iron after a careful

annealing and obtained a maximum permeability of 5490 and a hysteresis loss of 2450 ergs per cu. cm. per cycle at a B_{max} of 9000. At the same B_{max} Ewing[68] obtained a permeability of 4090 and a hysteresis loss of 2310 ergs per cu. cm. per cycle on a Swedish transformer iron.

111. Investigation of Magnetic Properties, 1900–1910.—The classic work of Barrett, Brown, and Hadfield[100] on the electric and magnetic properties of iron and iron alloys resulted in the development and commercial use of silicon transformer steel. Their purest material, a Swedish charcoal iron, previously referred to in the discussion of electric resistivity, had a maximum permeability of 3700; for B_{max} = 17,700 the coercive force was 1.10 oersteds, the residual induction 10,800 gausses, the hysteresis loss 8754 ergs per cu. cm. per cycle. This material was inferior magnetically to some iron-silicon and iron-aluminum alloys.

The properties of a number of commercial irons and steels were investigated by Gumlich and Schmidt[102] in 1901. Their best material, sheet iron, had a residual induction of 10,300 gausses, a coercive force of 0.60 oersted, and hysteresis loss of 4900 ergs per cu. cm. per cycle at B_{max} = 18,190. The maximum permeability was 8350.

The magnetic properties of the reduced iron prepared by Kreusler from ferrous oxalate were reported by Gumlich[177] in 1908 to be much inferior to those of an annealed dynamo steel, as follows:

Property	Kreusler reduced iron	Annealed dynamo steel
Maximum permeability....................	2,260	14,200
Coercive force, for H_{max} = 138, oersteds......	2.58	0.37
Residual induction for H_{max} = 138, gausses...	12,250	11,050
Hysteresis loss, for H_{max} = 138, ergs per cu. cm. per cycle..........................	20,100	3,760

The following year Gumlich[194,195] reported magnetic characteristics of an electrolytic iron which contained a total of 0.045 per cent of reported impurities (0.024 per cent carbon, 0.004 per cent silicon, 0.008 per cent manganese, 0.008 per cent phosphorus,

and 0.001 per cent sulphur). The values reported for this material for $H_{max.} = 6500$ were:

Property	Unannealed	Annealed 24 hr. at 800°C. (1470°F.)
Coercive force, oersteds.........	2.82	0.375
Residual induction, gausses......	11,440	10,850
Maximum permeability.........	1,850	14,600
Steinmetz coefficient η..........	0.00308	0.00078
Saturation value $(4\pi I)$..........	21,620	21,630

Saturation intensity of magnetization $I_\infty = 1719$.

The intensity of magnetization at saturation for Swedish iron was reported by Weiss[171] in 1907 as 1731. In 1910 Weiss[227] determined the same property on Swedish iron and also on Merck's electrolytic iron and Kreusler's reduced iron. The best value, 1706, was obtained on the Swedish iron.

112. Investigations of Magnetic Properties, 1910–1920.—The magnetic properties of the electrolytic iron produced by Burgess and Aston[208] were investigated in 1910. The iron was melted in a carbon resistance furnace and the ingots forged into rods. There was a pickup of impurities, particularly carbon, in the process; the carbon content of different rods varied from 0.012 to 0.120 per cent. Hence considerable variation was found in magnetic properties, which were somewhat inferior to those of sheet steel used for electric purposes. Terry[225] obtained a maximum permeability of 11,000 for Burgess and Aston electrolytic iron annealed at 1100°C. (2010°F.), the iron being incased in electrolytic-iron powder during the annealing to prevent oxidation. The hysteresis loss of this iron was 4900 ergs per cu. cm. per cycle, the residual induction 12,800 gausses, and the coercive force 0.53 oersted for $H_{max.} = 80$ oersted. In 1913 Breslauer[270] reported the maximum permeability of annealed Fischer electrolytic iron as 11,500, the hysteresis loss as 1440 ergs per cu. cm. per cycle. The induction value used was not stated.

The first of the many contributions of Yensen[321] to the knowledge of the magnetic properties of iron appeared in 1914. By

TABLE 41.—Magnetic Characteristics of Open-hearth Ingot Iron*

Condition	Maximum permeability	Induction for μ_{max}, gausses	For B_{max} = 10,000				For B_{max} = 15,000		
			Permeability	Hysteresis loss, ergs per cu. cm. per cycle	Residual induction, gausses	Coercive force, oersteds	Hysteresis loss, ergs per cu. cm. per cycle	Residual induction, gausses	Coercive force, oersteds
As received........	7,250	10,000	7,250	...	9,000	0.85	5,550	13,000	1.0
Vacuum melted........	17,000	9,000	16,700	852	8,400	0.28	1,755	12,600	0.33
Vacuum melted........	20,900	9,000	20,200	865	9,300	0.30	1,760	13,600	0.34

* Yensen.[110]

melting electrolytic iron in vacuum, material was produced with maximum permeability as high as 19,000, hysteresis loss 813 ergs per cu. cm. per cycle for $B_{max.}$ = 10,000, and 1640 ergs per cu. cm. per cycle for $B_{max.}$ = 15,000. The coercive force was 0.29 oersted and the residual induction 12,100 gausses, both for $B_{max.}$ = 15,000. In 1915 Yensen[341] reported values for electrolytic iron as follows: Maximum permeability 25,800, induction for $\mu_{max.}$ 9000 gausses; for $B_{max.}$ = 10,000, permeability was 25,600, hysteresis loss 707 ergs per cu. cm. per cycle, residual induction 9300 gausses, and coercive force 0.23 oersted. The following year Yensen[360] reported the magnetic properties of basic open-hearth ingot iron before and after melting in vacuum. Some of Yensen's data on this material are given in Table 41.

A saturation intensity of magnetization of 1798 and a coercive force of 0.36 oersted were reported by Williams[340] in 1915 for vacuum-melted electrolytic iron. Gumlich[387] in 1918 reported 21,620 for the saturation value $(4\pi I_\infty)$ of Fischer electrolytic iron and 21,328 for Swedish charcoal iron. Gumlich[387] also gave the following values for unannealed and annealed electrolytic iron:

Treatment	For $H_{max.}$ = 130		Maximum permeability
	Coercive force, oersteds	Residual induction, gausses	
Unannealed............................	2.83	11,450	1,850
Vacuum annealed for 24 hr. at 800°C. (1470°F.), cooled slowly............	0.375	10,850	14,400
Five heatings at 920°C. (1690°F.), with rapid cooling......................	0.225	5,000	11,600
Thirteen heatings at 830°C. (1525°F.), with rapid cooling.................	0.155	850	4,800

113. Recent Investigations of Magnetic Properties.—Further data on the magnetic characteristics of electrolytic iron after annealing at temperatures between 770 and 1100°C. (1420 and 2010°F.) were given by Gumlich[434] in 1921. The best values obtained, not all on the same specimen, were: coercive force

0.115 oersted, residual induction 1640 gausses (both for $H =$ 150), saturation induction 21,490, initial permeability 410. Fukuda[558] found that vacuum-melted electrolytic iron, when rolled into sheets, did not show the high permeability of the iron in the form of bars. According to Yensen,[590] this was due to oxidation and grain refinement in the preparation of the sheets.

Yensen[590] in 1924 made an exhaustive study of the magnetic properties of electrolytic iron and iron-carbon, iron-manganese, iron-silicon, iron-sulphur, and iron-phosphorus alloys, prepared with electrolytic iron as the base. Values from 4 of the 27 specimens of electrolytic iron are given in Table 42.

TABLE 42.—MAGNETIC PROPERTIES OF ELECTROLYTIC IRON*

Sample No.	Annealing temperature		Maximum permeability	Saturation induction,† gausses	For $B = 10,000$ gausses		
	°C.	°F.			Hysteresis loss, ergs per cu. cm. per cycle	Residual induction, gausses	Coercive force, oersteds
2–210	920	1688	16,000	22,400	1,060	9,000	0.32
2–210	1142	2088	33,000	22,950	610	9,350	0.20
2–210	1093	2000	41,500	23,050	505	9,400	0.17
2–231 N	910	1670	25,000	......	517	8,700	0.15

* Yensen.[590]
† In a private communication Yensen stated that these saturation values are probably too high. They were obtained by extrapolation, using Kennelly's law; this procedure is now believed to give high results.

In 1928, Yensen[813] reported the following magnetic characteristics for electrolytic iron, vacuum melted with addition of a small amount of carbon to remove oxygen, and then forged and machined into rings which were annealed at 900°C. (1650°F.):

Maximum permeability........................ 61,000
Initial permeability........................... 1,150
Hysteresis loss for $B = 10,000$, ergs per cu. cm. per cycle..................................... .300
Coercive force for $B = 10,000$, oersteds......... 0.09

A recent development in the production of iron of improved magnetic qualities is the treatment in hydrogen at high temperatures, first proposed by Cioffi.[876,964] Basic open-hearth ingot

iron was treated with moist hydrogen for 18 hr. at 1475°C. (2685°F.), then cooled to 880°C. (1615°F.) in 1 hr., annealed at 880°C. (1615°F.) for 17 hr. and slowly cooled to room temperature. The magnetic characteristics reported by Cioffi for the hydrogen-treated iron were:

Maximum permeability...................... 180,000
Initial permeability......................... 4,000
Hysteresis loss ($B_{max.}$ = 14,000), ergs per cu. cm. per cycle............................. 190
Coercive force ($B_{max.}$ = 14,000), gausses....... 0.025

Subsequent vacuum treatment of the iron at high temperature caused evolution of a volume of gas equal to one-half the volume of the iron. The analysis of the gas evolved was approximately 21 per cent H_2, 33 per cent CO_2, 34 per cent CO, 2 per cent N_2, and 10 per cent H_2O. Prolonged vacuum treatment reduced the maximum permeability from 190,000 to 145,000 but this may have been due to contamination even in the very high vacuum or to a reduction in thickness of the metal as a result of volatilization. Magnetic characteristics are to some extent dependent upon the cross section of the metal.

Figure 36 shows some recent results, which were obtained by Cioffi, for the permeability of hydrogen-treated iron as compared with the permeability of the same material in the annealed condition but not subjected to the hydrogen treatment. The curve was published in the recent review by Ellis and Schumacher.[1052]

By using pure hydrogen and avoiding contamination from furnace gases during the treatment, Cioffi[1049] has increased the initial permeability to 14,000 and the maximum permeability to 280,000. These results are now attributed entirely to purification of the metal, not to absorbed hydrogen. The treatment reduces the content of oxygen, carbon, nitrogen, and sulphur to a few thousandths of 1 per cent each but has practically no effect on the content of metallic impurities. Introduction of nitrogen or of sulphur into hydrogen-treated iron reduces the permeability. After the addition of nitrogen, treatment in hydrogen at 1200°C. (2190°F.) is adequate to restore the former magnetic characteristics, but, after the addition of sulphur, similar heat treatment above 1300°C. (2370°F.) is required. Values for the properties other than the permeability of this material are not yet available.

There are few data available on the magnetic properties of carbonyl iron although the report of Duftschmid, Schlecht, and Schubardt[965] indicates that the magnetic properties of this material are somewhat superior to those of electrolytic iron. These authors reported the following characteristics for carbonyl
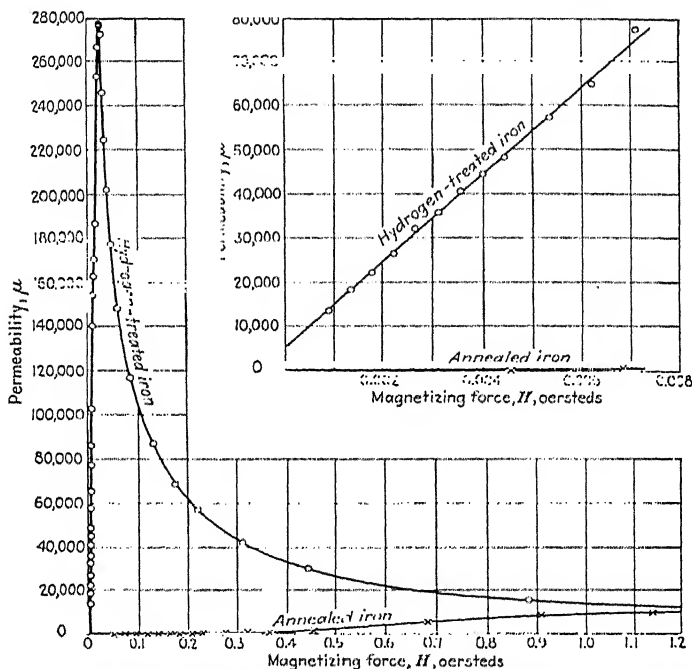
Fig. 36.—The effect of hydrogen treatment on the permeability of annealed iron. (*Cioffi, according to Ellis and Schumacher.*[1052])

iron: Maximum permeability of 20,000, saturation induction of 22,000 gausses, residual induction of 6000 gausses for a B_{max} of 10,000, and coercive force of 0.08 oersted, also for a B_{max} of 10,000. Carbonyl iron is being used in some of the investigations, which are now in progress, of the effect of hydrogen treatment on the magnetic properties, but the results of these investigations are not yet available.

Results representing the magnetic properties of different forms of high-purity iron, from the work of various investigators, are assembled in Table 43.

TABLE 43.—MAGNETIC PROPERTIES OF HIGH-PURITY IRON

Material	Investigator	Date	Reference	Maximum permeability	Saturation induction, gausses	For $B_{max.}$ = 10,000		
						Hysteresis loss, ergs per cu. cm. per cycle	Residual induction, gausses	Coercive force, oersteds
Electrolytic iron	Yensen	1915	341	25,800	......	707	9,300	0.23
	Yensen	1924	590	41,500	23,050	505	9,400	0.17
	Yensen	1928	813	61,000	......	300	.....	0.09
	Gumlich	1918	387	....	21,620			
	Gumlich	1921	434	....	21,490	...	1,640	0.115
Basic open-hearth ingot iron	Yensen	1916	360	7,250	......	...	9,000	0.85
Carbonyl iron	Duftschmid, Schlecht, and Schubardt	1932	965	20,000	22,000	...	6,000	0.08
Hydrogen-treated iron	Cioffi	1934	1049	280,000	......	190*	.....	0.025

* $B_{max.}$ = 14,000.

B. EFFECT OF TEMPERATURE

A change in temperature has a pronounced effect on the magnetic properties of iron. The magnetic properties of the different allotropic modifications differ in nature as well as in degree; there is a magnetic transition in the properties of alpha iron at the A_2 point; the properties of the other allotropic forms are affected by changes in temperature within the ranges of their existence.

114. Magnetic Properties of Alpha Iron at Low Temperatures. An early investigation of the magnetic properties of iron at low temperatures was made by Fleming and Dewar,[69] who found that the permeability at low temperatures was less than at room temperature for annealed Swedish iron, but was greater for the unannealed hardened iron. The hysteresis loss was independent of temperature. Honda and Shimizu,[132] however, found that

with decreasing temperature the permeability and hysteresis loss decreased for small fields but increased for large fields. Terry[225] studied the effects of temperature on the magnetic properties of Burgess' electrolytic iron. His data for the permeability of annealed specimens at low temperatures for different field strengths are given in Table 44; the hysteresis constants at low temperatures are given in Table 45.

TABLE 44.—PERMEABILITY OF ANNEALED ELECTROLYTIC IRON AT LOW TEMPERATURES[*]

Temperature		Field strength, oersteds								H for maximum permeability
°C.	°F.	0.2	0.5	1	1.5	2	3	10	60	
−190	−310	60	90	100	140	190	430	1130	286	6.9
−121	−186	65	120	250	250	700	1000	1200	284	5.4
− 60	− 76	70	190	400	400	1100	1800	1300	283	4.2
+ 23	+ 73	80	260	500	870	1900	2600	1400	281	2.9

[*] Terry.[225]

TABLE 45.—HYSTERESIS CONSTANTS OF IRON AT LOW TEMPERATURES[*]

Temperature		Hysteresis loss for $H = \pm 90$, ergs per cu. cm. per cycle	Maximum induction, gausses	Residual induction, gausses	Coercive force, oersteds
°C.	°F.				
−190	−310	26,900	17,600	11,300	4.00
−170	−274	24,150	17,600	12,300	3.55
− 60	− 76	21,200	17,500	13,200	2.97
+ 23	+ 73	17,490	17,400	13,600	2.31

[*] Terry.[225]

115. Magnetic Properties of Alpha Iron at Elevated Temperatures.—The first important work on the magnetic properties of iron at elevated temperatures in the alpha iron range was that of Hopkinson[45] on wrought iron in 1889. With small fields (0.3 oersted) the permeability increased slowly with temperature to about 640°C. (1185°F.), then rose rapidly to a maximum of about 11,000 at 727°C. (1340°F.) and then decreased to approximately unity at 737°C. (1360°F.). At a magnetizing force of 4.0 oersteds the permeability was nearly constant (2500 to 2750)

to about 600°C. (1110°F.) and then decreased rapidly to approximately unity. During the next two decades much work was done on the magnetism-temperature relationship of commercial forms of iron.

Terry[225] found that the hysteresis loss, retentivity, and coercivity of Burgess' electrolytic iron decreased with increasing temperature. With low fields the permeability showed a sudden
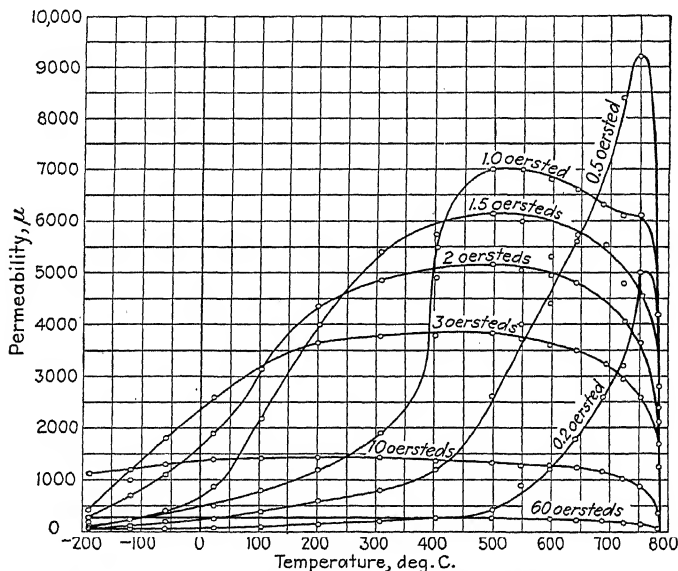
Fig. 37.—Variation of the permeability of annealed electrolytic iron with temperature. (*Terry.*[225])

rise to a maximum at a temperature slightly below the Curie point, the amount of this rise decreasing with increasing fields. Terry's data are shown in Figs. 37 and 38.

116. Magnetic Properties above the A_2 Point.—The temperature of the magnetic transformation, the A_2 point, has been discussed in the consideration of the allotropy of iron (see Chap. 4). Methods such as thermal analysis determine the temperature at which the transition is most rapid, whereas the magnetic A_2 point is generally considered to be the temperature above which ferromagnetism is no longer detectable. Thermal-analysis

methods indicate that the A_2 point occurs at about 768°C. (1415°F.); the magnetic A_2 point, the Curie point, is usually given as between 780 and 800°C. (1435 and 1470°F.) although temperatures both higher and lower are found, depending upon the material and the sensitivity of the instruments used.

Although ferromagnetism is no longer detectable at temperatures above the Curie point, iron is paramagnetic above this temperature. Curie[64] showed that the susceptibility of iron above the A_2 point is a small but definite value. The mass
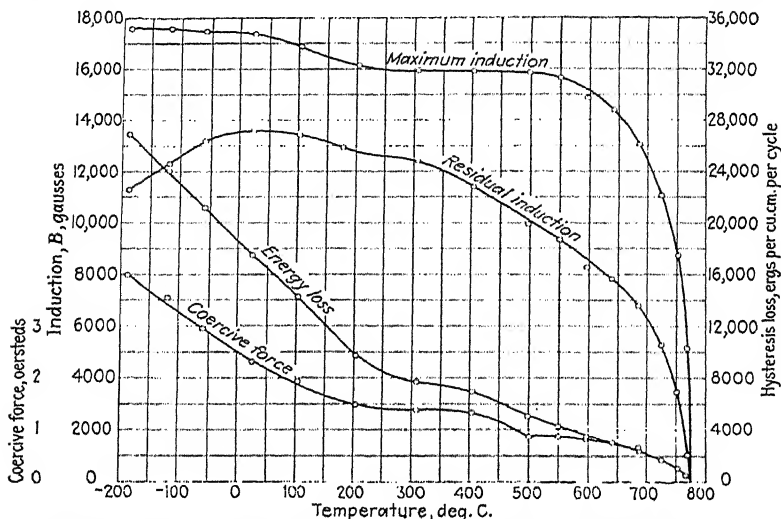
Fig. 38.—Variation of the hysteresis constants of annealed electrolytic iron with temperature. (*Terry.*[225])

susceptibility of paramagnetic alpha iron as reported by Honda and Takagi,[331] Terry,[384] and Ishiwara[416] is shown in Fig. 39. The data were obtained on electrolytic iron; Terry used Burgess' electrolytic iron which had been melted in a vacuum in a magnesia crucible.

117. Magnetic Properties of Gamma Iron.—Five determinations of the mass susceptibility of iron in the gamma range have been reported. Honda and Takagi[243] used an ingot which was prepared by electric melting of Kahlbaum's "pure" powdered iron. Electrolytic iron was used by Terry[384] and in two
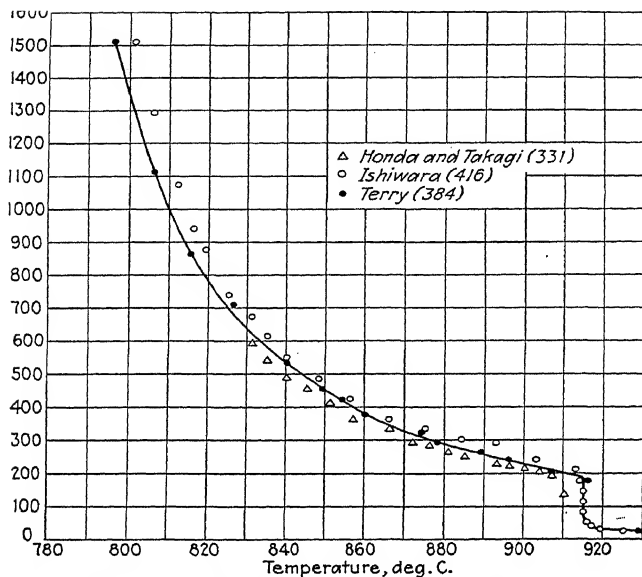
FIG. 39.—Mass susceptibility of alpha iron above the Curie point.
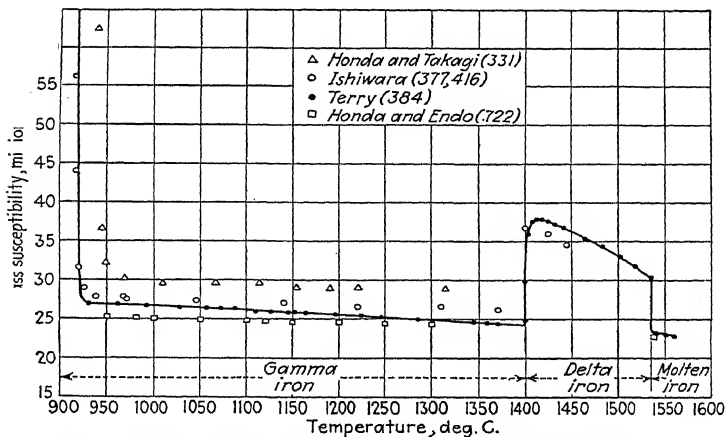
FIG. 40.—Mass susceptibility of gamma, delta, and molten iron.

investigations by Ishiwara.[377,416] Honda and Endo[722] used basic open-hearth ingot iron. The results of these determinations of the susceptibility of gamma iron are summarized in Fig. 40.

118. Magnetic Properties of Delta Iron.—Curie[64] noted the increase in susceptibility at the A_4 point, but the temperature of this effect was reported as about 1280°C. (2335°F.), owing to the inaccurate pyrometry of that time. The data reported by Ishiwara[377] and Terry[384] for electrolytic iron indicate that the susceptibility of delta iron decreases with temperature, as shown in Fig. 40.

119. Magnetic Properties of Liquid Iron.—Honda and Endo[722] stated that the mass susceptibilities of molten iron and steel were between 22 and 23.5 × 10⁻⁶. Terry made measurements of susceptibility on unannealed electrolytic iron which he stated began to melt at about 1500°C. (2730°F.). From his curve the following values for the mass susceptibility of liquid iron were obtained:

Temperature, °C..................	1520	1530	1540	1550	1560
Mass susceptibility, millionths......	23.7	23.5	23.3	23.1	22.9

C. EFFECT OF IMPURITIES

The effect of impurities on the magnetic properties was summarized by Yensen[989] in the form of a curve which showed the changing values, for maximum permeability, reported from year to year. In the years prior to 1900, magnetic measurements were made on relatively impure irons; the magnetic properties of electrolytic iron produced between about 1900 and 1913 were found to be definitely superior to those of less pure specimens previously used; since 1913, investigators such as Yensen[989] and Cioffi[964,1049] have shown that permeabilities previously undreamed of can be obtained from high-purity irons. The extraordinarily high permeability attained in recent years may be ascribed in part to treatments which are not strictly purification processes; nevertheless the fact that the best results have been obtained by treating specimens which were originally of high purity indicates that purity is one of the important factors in

determining the magnetic properties. Yensen's permeability curve, with the addition of recent data obtained by Cioffi, is shown in Fig. 41. A companion curve, for the change in the hysteresis loss in iron, from year to year since 1885, is shown in Fig. 42.
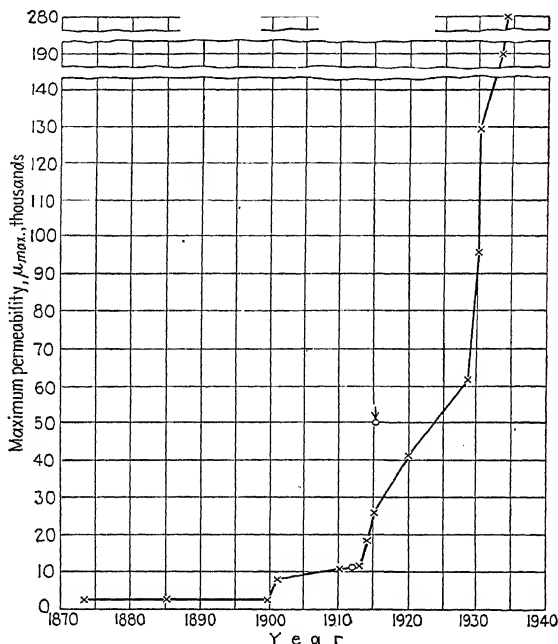
Fig. 41.—Maximum permeability of iron as reported since 1873. (*Yensen*[989] and *Cioffi.*[1049])

In considering the effect of impurities, Yensen[989] assumed that the magnetic properties depend upon the regularity of the crystal lattice and that elements may be divided into two classes according to their effect upon the lattice and therefore upon the magnetic properties. Small amounts of elements such as nickel, cobalt, silicon, and aluminum, which substitute for iron atoms, cause little strain in the lattice and therefore relatively little change in the magnetic properties. Elements such as carbon, oxygen, nitrogen, and sulphur do not substitute for iron

atoms but occupy positions between the iron atoms; these elements distort the lattice in occupying the interstitial spaces and exert a detrimental effect upon the magnetic properties. They may also react with interstitial elements and precipitate them from solution, thus exerting an indirect effect on the magnetic properties.[954]

The phenomenon of magnetic aging, the change with time of magnetic properties of cold-worked or quenched metal, is also an effect of impurities. It results from the gradual precipitation of impurities from solid solution. There is little information
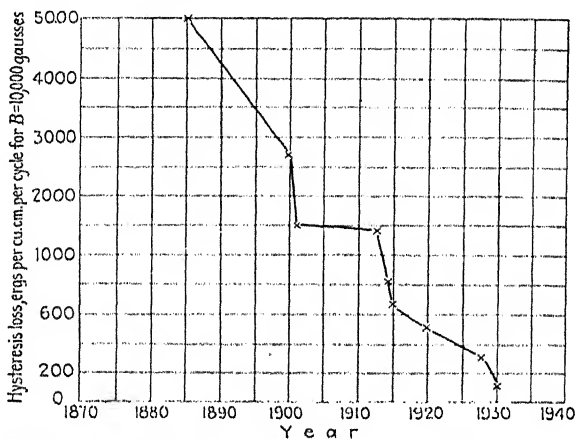
Fig. 42.—Hysteresis loss of iron as reported since 1885.   (*Yensen.*[989])

available in regard to magnetic aging in high-purity irons, but it would be expected that this effect would decrease in importance with increasing purity of the material.   Köster[838] found that the coercive force of either Armco iron or Swedish iron, which had been quenched from 930°C. (1705°F.), was approximately doubled by 14 days' aging at 100°C. (210°F.), but the coercive force of electrolytic iron was not affected by this treatment.

Available knowledge of the effect of impurities on the magnetic properties of iron is due largely to two investigators, Yensen and Gumlich.   The former used electrolytic iron as the base in preparing his alloys which, therefore, contained only slight amounts of elements other than iron and the alloying element;

Gumlich used commercial irons and steels containing considerable amounts of impurities which probably influenced to some extent the effect of the varying element in the series. Consequently Yensen's data seem more reliable at least as regards the effect of small amounts of impurities.

120. Effect of Aluminum.—The saturation induction of iron-aluminum alloys may be expressed, according to Gumlich,[387] by the equation:

$$\text{Saturation induction } (4\pi I_\infty) = 21,640 - 570 \times \% \text{ Al}$$

121. Effect of Carbon.—The effect of carbon on the saturation intensity was studied by Gumlich[387] who found that different equations were necessary to express the effect of variations in the carbon content above and below 0.96 per cent. Carbon affects the magnetic properties of iron to a marked extent according to Yensen's[590] data for the iron-carbon alloys, abstracted in Table 46.

TABLE 46.—EFFECT OF CARBON ON MAGNETIC CHARACTERISTICS*

Carbon, per cent	Maximum permeability	Saturation† induction, gausses	For $H_{max.}$ = 10,000		
			Hysteresis loss, ergs per cu. cm. per cycle	Residual induction, gausses	Coercive force, oersteds
0.0015	41,500	23,050	505	9,400	0.17
0.0017	27,300	......	647	8,400	0.21
0.0018	24,000	......	660	9,000	0.20
0.0025	20,000	......	873	8,200	0.28
0.0040	12,000	......	1,440	8,950	0.48
0.008	9,000	22,800	1,700	8,100	0.58
0.021	5,400	22,650	2,070	7,000	0.67
0.061	4,670	22,600	2,150	6,550	0.76
0.174	3,300	......	3,120	6,900	1.00

* Yensen.[590]

† These saturation values are probably too high. See footnote to Table 42, p. 218.

These data indicated to Yensen that the effect on the magnetic properties differed greatly in different ranges of carbon content. The effect of very small amounts, less than 0.008 per cent, was to increase the hysteresis loss by an amount equal to 104,000

times the percentage of carbon. For carbon contents between
0.008 and 0.09 per cent the effect of increasing carbon was not so
pronounced; it was the effect of 0.008 per cent of carbon plus
an amount equal to 2250 times the percentage of carbon in
excess of 0.008 per cent. The effect again increased for carbon
contents between 0.09 and 0.9 per cent; within this range the
effect was that of 0.09 per cent of carbon plus an amount equal
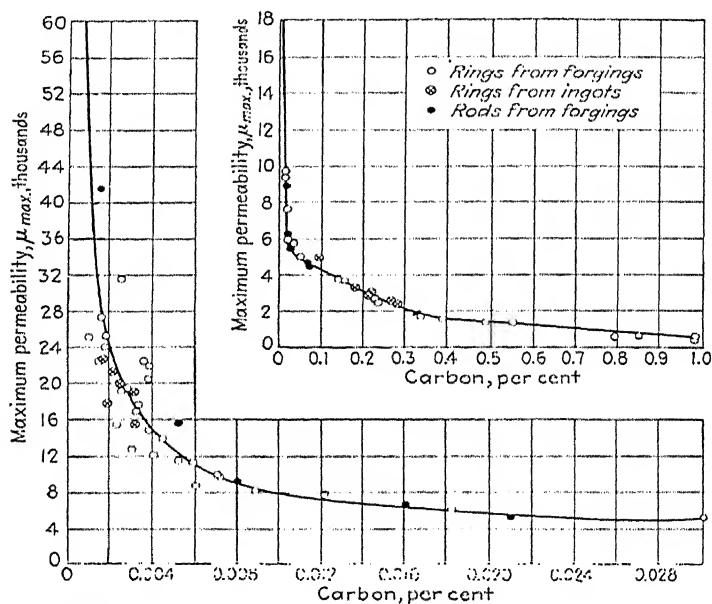
Fig. 43.—Effect of carbon content on the maximum permeability of iron.
(*Yensen.*[590])

to 16,700 times the percentage of carbon in excess of 0.09 per cent.
Yensen suggested that these effects were due to the different
forms in which carbon exists in iron: for carbon contents of less
than 0.008 per cent the carbon was in solid solution in the iron;
between 0.008 and 0.09 per cent the carbon existed as cementite,
and between 0.09 and 0.9 per cent as pearlite. Evidently the
carbon which is in solid solution in iron is particularly potent
in affecting magnetic properties. As Yensen suggested, the

beneficial effects of additions of silicon to iron, with respect to the magnetic properties, are due at least in part to changes in the state of existence of the carbon, to precipitation of carbon as graphite instead of as pearlite. It is also possible that the presence of silicon decreases the amount of carbon which can be retained in solid solution in the iron.
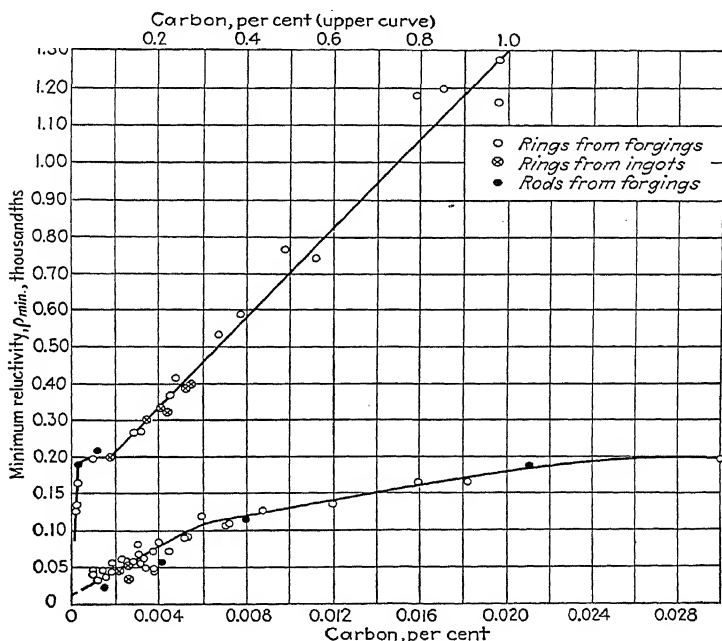
Fig. 44.—Effect of carbon content on the minimum reluctivity of iron.
(*Yensen.* (590))

The relation between maximum permeability and carbon content was a rectangular hyperbola for low carbon contents (Fig. 43), according to Yensen; the relation between minimum reluctivity, which is the reciprocal of maximum permeability, and carbon content was a straight line (Fig. 44). Recently Yensen and Ziegler[1081] extended this work and determined the effect of small amounts of carbon and of oxygen on the magnetic properties of ring samples of selected electrolytic iron.

The amounts of impurities present, other than carbon and oxygen, were low and were uniform. The contents of phosphorus, manganese, and sulphur were each less than 0.003 per cent, hydrogen was 0.001 per cent or less, and nitrogen 0.0005 per cent or less. It was found that the effect of 0.001 per cent of
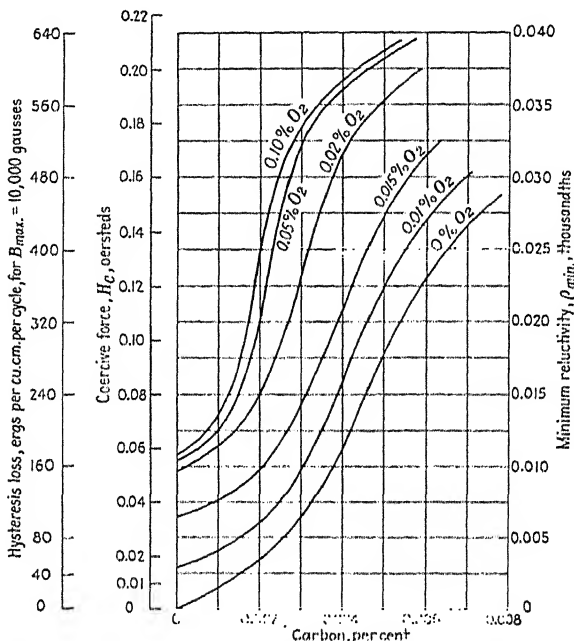
Fig. 45.—Effect of carbon content on the magnetic properties of iron. (*Yensen and Ziegler.*[1011])

carbon was about 10 times that of an equal amount of oxygen and that the effects of carbon and oxygen were interrelated. These new data indicated that the effect of carbon in oxygen-free iron was not so great as was indicated in the earlier work[590] with samples which contained about 0.02 per cent of oxygen. The new data of Yensen and Ziegler for the effects of small amounts of carbon on the hysteresis loss and coercive force for a $B_{max.}$ of 10,000 and on the minimum reluctivity are shown in Fig. 45; the effect of carbon on the maximum permeability of a

single crystal of oxygen-free iron is shown in Fig. 46. These data indicate that the maximum permeability of a single crystal of iron, which contained 0.001 per cent of carbon and was free from oxygen, would be about 500,000.
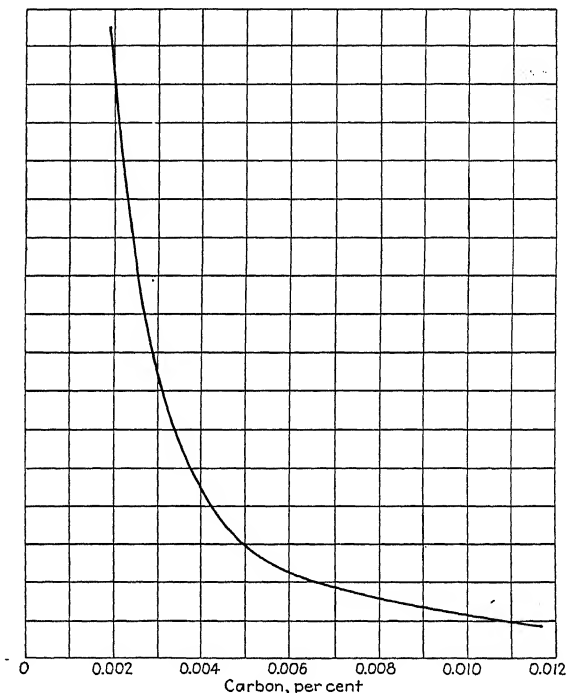
FIG. 46.—Effect of carbon content on the maximum permeability of a single crystal of oxygen-free iron. (*Yensen and Ziegler.*[1081])

The magnetic characteristics of a series of iron-carbon alloys prepared from electrolytic iron were determined by Cheney.[464] These alloys were essentially carbon steels, with carbon contents up to 1.60 per cent; consequently discussion of Cheney's results is beyond the scope of this monograph.

122. The Effect of Hydrogen.—The earliest investigations of the magnetic properties of electrolytic iron were on iron as deposited. Such iron usually contains appreciable amounts of

occluded hydrogen which makes it hard magnetically as well as mechanically. Beetz[12] in 1860 reported that electrolytic iron deposited in a magnetic field had a large residual magnetism. Holz[28] reported similar results. Leick[71] used different electrolytes and found that the magnetic properties of the iron were independent of the electrolyte, although later workers, Maurain,[104] Schild,[185] Kaufmann and Meier,[244] and Soné[339] found that the composition of the electrolyte, particularly acidity, had a marked effect on the magnetic properties of the iron. Leick[71] found the permanent magnetism to be about 70 per cent
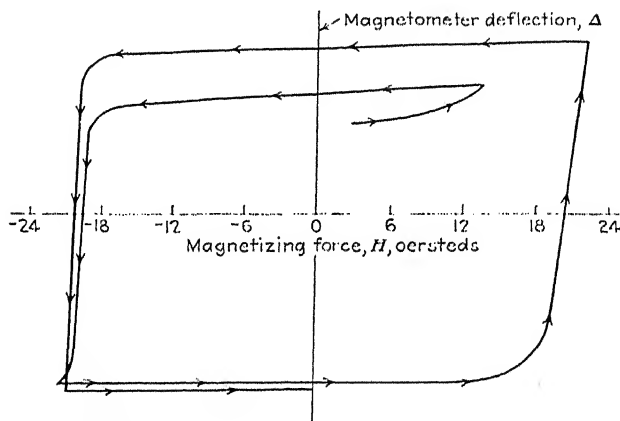
Fig. 47.—Hysteresis loop of cathode electrolytic iron. (*Maurain.*[104])

of the temporary value. Maurain[104] studied the relation between the magnetism of electrolytic iron and the strength of the field applied during electrodeposition. He found that the residual magnetism of iron deposited in a magnetic field was greater than that of iron deposited in zero field and then magnetized. These results were confirmed by Soné,[339] but Kaufmann and Meier[244] found that the magnetic properties were similar whether the iron was magnetized during deposition or after. Maurain[104] found that the hysteresis loop of electrolytic iron as deposited was much wider than that of ordinary iron and was in fact nearly a square with two opposite corners rounded, as is illustrated in Fig. 47. Kaufmann and Meier found that Maurain's

loop was obtained only when the composition of the electrolyte used in preparing the iron was kept within narrow limits. They also found that electrolytic iron gradually lost its peculiar magnetic properties upon standing, and concluded that this was due to a loss of occluded hydrogen, as the properties could be restored by cathodic polarization.

Some magnetic characteristics of electrolytic iron as deposited were reported by Burgess and Taylor,[141] Burgess and Aston,[208] Schild,[185] and Terry[225] and are given in Table 47.

TABLE 47.—MAGNETIC PROPERTIES OF ELECTROLYTIC IRON AS DEPOSITED

Investigator	Field strength, oersteds	Hysteresis loss, ergs per cu. cm. per cycle	Residual induction, gausses	Coercive force, oersteds	Maximum induction, gausses	Maximum permeability
Burgess and Taylor[141]	100	......	......	.....	15,750	
	200	......	10,300	11.0		
Burgess and Aston[208]	100	......	......	.....	17,450	
	200	......	11,200	18.5		
Schild[185]	24.6	7,442	......	.....	5,627	
	79.9	40,000	......	.....	13,105	
	123.8	56,900	......	.....	15,773	
Terry[225]	100	21,300	7,940	3.84	17,800	
	140	41,400	9,650	7.53	17,450	1,040

Recent investigations have shown that the effect of hydrogen on the magnetic properties of electrodeposited iron is due primarily to the distortion of the lattice which accompanies its introduction. Wever and Pfarr[1038] found that soft ingot steel (0.01 per cent carbon, 0.35 per cent manganese, 0.031 per cent phosphorus, 0.023 per cent sulphur, trace of silicon) contained about 30 cu. cm. of hydrogen per 100 g. of steel after electrolysis in dilute sulphuric acid, and that the introduction of this amount of hydrogen caused an increase in the width of the lattice, which increase was slowly reduced on standing as follows:

Condition of Material	Lattice Constant, Å.
Before electrolysis	2.8609
Immediately after electrolysis	2.8614
1 day after electrolysis	2.8614
5 days after electrolysis	2.8613
14 days after electrolysis	2.8611
15 days after electrolysis	2.8611

Reber[1070] concluded that the direct cause of the magnetic hardening of cathode iron was plastic deformation produced by internal liberation of hydrogen from the supersaturated metal. He found that recrystallization was necessary to remove the effects of the hydrogen; annealing at low temperatures, which removed the hydrogen but did not promote recrystallization, was ineffective. This conclusion, that the presence of hydrogen which is occluded in iron at ordinary temperatures is not the direct cause for the change in magnetic properties, agrees with the opinion which is now generally held in regard to the effect of the treatment of solid iron in hydrogen at high temperatures. The effect of the latter treatment is believed to be due to the increased purity and to grain refinement, not to the presence of residual hydrogen. It has been shown that iron, which has been treated under conditions which produce the maximum permeabilities so far obtained, does not retain more than the merest trace of hydrogen. Furthermore, Körber and Ploum[1011] found that some iron absorbed hydrogen during electrolysis but that residual hydrogen could not be detected in extremely pure iron after such treatment.

123. Effect of Manganese.—The hysteresis loss of electrolytic iron was increased by manganese by an amount equal to 1000 times the percentage of manganese according to Yensen.[590] This applied to contents of 0.6 per cent or less. Gumlich[387] expressed the effect on the saturation intensity of manganese up to 7.8 per cent by the equation:

$$\text{Saturation induction } (4\pi I_\infty) = 21{,}425 - 210 \times \% \text{ Mn}$$

124. Effect of Nitrogen.—Yensen[989] assumed that the effect of nitrogen would be similar to that of carbon, oxygen, and sulphur. A sample of Cioffi's hydrogen-treated iron contained only 0.0001 per cent nitrogen according to an analysis reported by Bain,[957] and it has been suggested that the production of high permeability is related to the elimination of nitrogen.

Some additional data on the effect of nitrogen were presented by Cioffi* showing that the permeability of a specimen of hydrogen-treated iron was diminished from 211,000 to 38,000 as a result of treatment in ammonia at 1200°C. (2190°F.). Subsequent treatment in pure hydrogen at 1200°C. increased the permeability
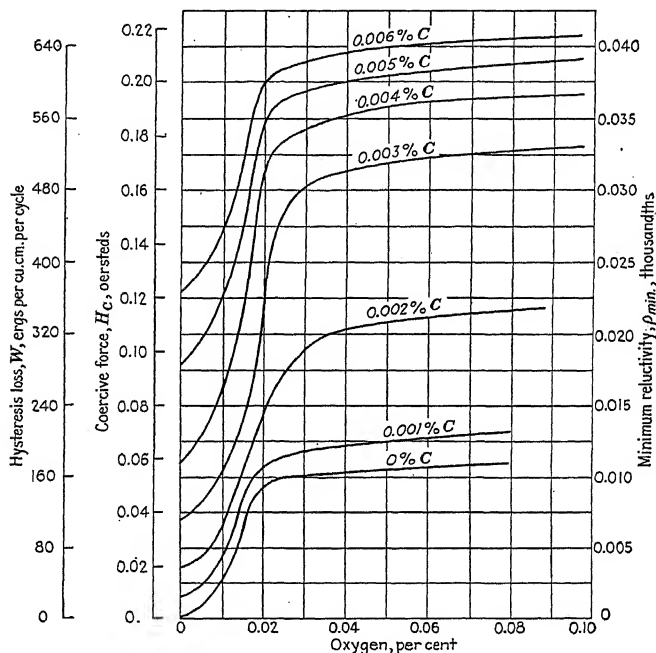
Fig. 48.—Effect of oxygen content on the magnetic properties of iron. (*Yensen and Ziegler.*[1081])

of this specimen to 280,000. Strauss[318] found that the magnetic properties of iron containing 4 per cent silicon were affected adversely by treatment at 600 and 900°C. (1110 and 1650°F.) with nitrogen.

125. Effect of Oxygen.—It has been generally assumed that oxygen is detrimental to the magnetic qualities of iron although there are few data available to show the quantitative relation between oxygen content and magnetic properties. This is due

* Data presented before the Am. Phys. Soc. in Washington, in April, 1934.

largely to the difficulty of obtaining specimens in which the oxygen content is the only variable. Gumlich[258] found that carbon monoxide was evolved from iron during an annealing process which resulted in an improvement in the magnetic properties. The work of Oertel and his coworkers[707,708] indicated that the best magnetic properties were produced by
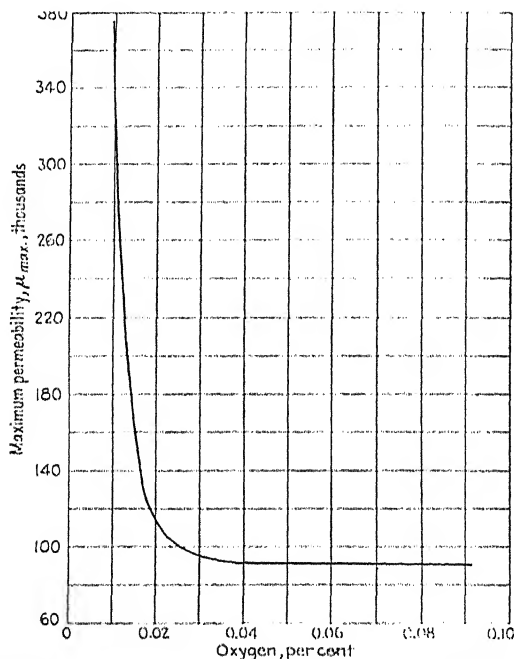
FIG. 49.—Effect of oxygen content on the maximum permeability of a single crystal of carbon-free iron. (*Yensen and Ziegler.*[1081])

annealing treatment when the iron prior to annealing contained carbon and oxygen in the relative proportions of the compound carbon monoxide. Gries and Esser[831] reported that an increase in the oxygen content of iron from 0.03 to 0.14 per cent increased the coercive force from 0.8 to 1.49 oersteds and increased the residual induction from 6400 to 11,500 gausses. Ziegler[1040] found that the maximum permeability decreased from 50,000 to

about 21,000 as oxygen increased from about 0.016 to 0.07 per cent.

Recent work by Yensen and Ziegler[1081] indicates that the effect of oxygen on the magnetic properties of iron is very large for contents of less than 0.02 per cent but that the effect of oxygen between 0.02 and 0.15 per cent (the limit of the investigation) is negligible. Some of their results for the effect of oxygen on hysteresis loss and coercive force at a $B_{max.}$ of 10,000, on minimum reluctivity, and on maximum permeability are shown in Figs. 48 and 49.

126. Effect of Phosphorus.—Phosphorus up to 0.015 per cent increased the hysteresis loss by an amount equal to 13,000 times the percentage of phosphorus, but further increase in the phosphorus content had no further effect on the hysteresis loss, according to Yensen.[590] He suggested that the limit of solubility of phosphorus in iron is 0.015 per cent and that larger amounts are precipitated as a non-magnetic compound with iron. Other determinations indicate that the limit of solubility

TABLE 48.—MAGNETIC PROPERTIES OF IRON-SILICON ALLOYS*

Silicon, per cent	Maximum permeability	For $B_{max.}$ = 10,000					For $B_{max.}$ = 15,000		
		Permeability	Hysteresis loss, ergs per cu. cm. per cycle	Residual induction, gausses	Coercive force, oersteds		Hysteresis loss, ergs per cu. cm. per cycle	Residual induction, gausses	Coercive force, oersteds
0.001	25,800	25,600	707	9,300	0.23		1,451	12,700	0.28
0.01	29,000	28,670	707	9,600	0.21		1,604	14,300	0.31
0.048	27,000	27,000	700	9,440	0.23		1,660	14,480	0.32
0.064	36,800	36,300	502	9,500	0.16		1,326	14,300	0.25
0.091	45,250	43,500	394	9,500	0.13		929	14,300	0.17
0.148	66,500	41 700	286	9,080	0.09		916	12,000	0.16
0.205	30,200	29,500	649	9,300	0.20		1,526	14,480	0.27
0.242	36,500	33,000	436	9,700	0.13		1,346	14,500	0.21
0.309	44,800	43,500	445	9,600	0.13		1,412	14,500	0.24
0.400	22,500	22,000	725	9,440	0.21		1,820	14,480	0.32
0.698	20,350	19,600	780	9,300	0.25		2,220	14,400	0.40
1.71	30,150	24,700	440	8,700	0.12		1,292	12,000	0.22
2.73	46,800	46,000	404	9,100	0.13		1,260	13,300	0.23
3.40	63,300	46,500	280	9,100	0.08		1,025	12,400	0.15
4.39	25,700	15,400	591	8,300	0.20		1,819	10,200	0.25
4.92	12,200	7,040	780	6,300	0.26		2,620	7,100	0.35

* Yensen.[342]

of phosphorus in iron is about 1 per cent at room temperature. (See discussion of phosphorus in Chapter XII of this monograph.)

127. Effect of Silicon.—Values of the saturation induction for iron-silicon alloys containing up to 5 per cent silicon were expressed by Gumlich[387] by the following formula:

$$\text{Saturation induction } (4\pi I_\infty) = 21,600 - 480 \times \% \text{ Si}$$

The magnetic properties of electrolytic iron alloyed with increasing amounts of silicon are given in Table 48 from Yensen's data.[342]

128. Effect of Sulphur.—Cioffi reported* that when hydrogen-purified iron, which had a μ_{max} of 123,000, was heated at 1300°C. (2370°F.) in hydrogen which contained 0.05 per cent of hydrogen sulphide, the permeability diminished to 39,000. Subsequent treatment in pure hydrogen at 1480°C. (2695°F.) restored the permeability to 144,000.

The only available data on the effect of sulphur on the hysteresis loss are those of Yensen,[590] who found that sulphur when present in amounts of 0.06 per cent or less, increased the hysteresis loss by an amount equal to 18,000 times the percentage of sulphur.

D. EFFECT OF GRAIN SIZE

As early as 1902 it was pointed out by Hicks[103] that the elements aluminum, silicon, and phosphorus, which increased the permeability of iron when alloyed with it, also increased the crystalline size of the metal. It was suggested that the increase in permeability was an effect of increased crystal size. Thompson[358] heat treated several samples of Swedish bar iron to produce material of different crystal size and found that the maximum induction and residual induction were independent of crystal size but that the coercive force and hysteresis loss increased with decreasing crystal size. Yensen[590,872] found that the relation between grain size and hysteresis loss was affected by the carbon content. For carbon in solution (less than 0.008 per cent) the relation was expressed by the equation

$$W = 65\sqrt{N} + K,$$

* Data presented before the Am. Phys. Soc. in Washington, in April, 1934.

where W = the hysteresis loss, N = the number of grains per sq. mm., and K = the correction for effect of impurities. For carbon contents over 0.008 the equation was: $W = 3N + K$.

Honda and Kaya[667] determined the magnetic characteristics of six specimens of Swedish mild steel (0.10 per cent carbon, trace of silicon, 0.40 per cent manganese, 0.021 per cent sulphur, and 0.021 per cent phosphorus) of varying grain size. Their results are given in Fig. 50. The value of $H_{max.}$ used was not stated. Von Auwers[762,763] investigated the magnetic properties of electrolytic-iron strips which were stretched to 2, 4, 7, 15,
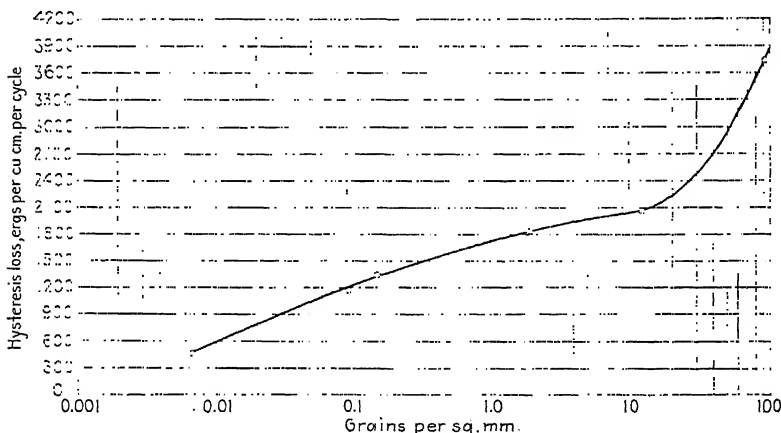
Fig. 50.—Relation between hysteresis loss and grain size of mild steel. (*Honda and Kaya.*[667])

and 25 per cent elongation and annealed at 870°C. (1600°F.) for 40 hr. The grain size varied from 4 sq. mm. to 0.050 sq. mm. Von Auwers concluded that grain size does not directly influence the magnetic properties but exerts an indirect influence on the effect of impurities localized on the grain surface.

The effect of grain size was investigated by Sizoo[806] for electrolytic iron which contained 0.024 per cent carbon, 0.014 per cent silicon, and 0.012 per cent sulphur. Since the effects of grain size might be masked by differences in thermal or mechanical treatment, Sizoo took precautions to have his specimens uniform except for grain size. From his results, Fig. 51, he

concluded that with increasing crystal size coercive force and hysteresis loss decreased, maximum permeability increased, and residual induction was unaffected. Gerlach[612] stated that the residual induction decreased with increasing crystal size. Results of an investigation by Ruder[1071] led him to conclude that, although grain size does affect the hysteresis loss, other factors
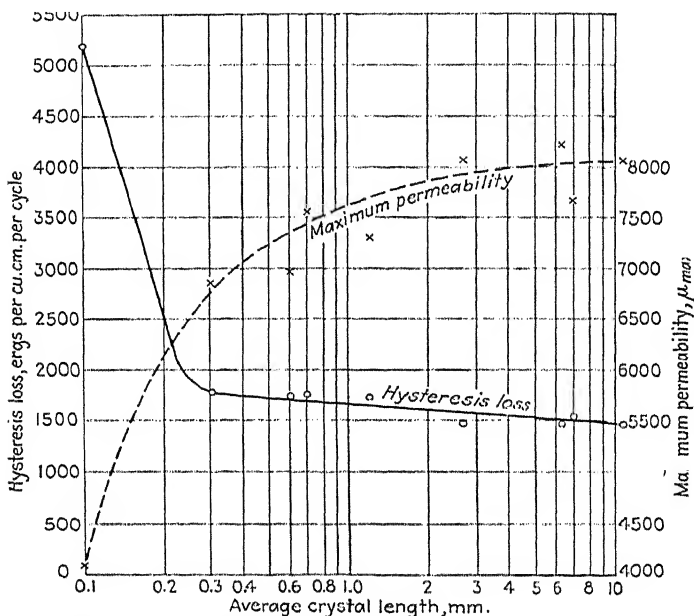
FIG. 51.—Effect of grain size of electrolytic iron on hysteresis loss and on maximum permeability. (*Sizoo*.[806])

such as purity, method of preparation, size and heat treatment of specimens have a much greater effect, so that variations in these factors may mask the effect of grain size.

The results obtained by Ziegler[913] showed a definite relationship between the magnetic quality of iron and grain size: the coarser the grain, the higher the magnetic quality. Recent work of Yensen and Ziegler[1081] showed that the effect of grain size on the magnetic properties, eliminating the effects of carbon and of oxygen, is proportional to the grain number N, not to the

square root of this number as reported in an earlier investigation.[590]   Their results are shown in Fig. 52.   They also found that the effect of grain size varies with the amounts of non-metallic elements which are present.

E. EFFECT OF COLD WORK AND HEAT TREATMENT

Since the magnetic properties of iron depend upon the regularity of the crystal lattice, any deformation, such as occurs in cold
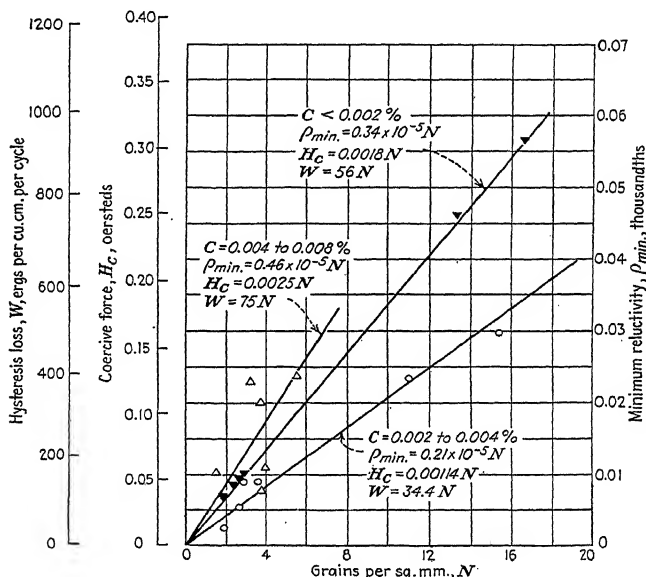
FIG. 52.—Effect of grain size, at different carbon contents, on the magnetic properties of iron.   (*Yensen and Ziegler.*[1081])

working or heat treatment, which induces strains in the crystal structure, affects the magnetic properties.

129. Effect of Cold Work.—Reference has been made previously in this chapter to the work of Reber[1070] who showed that the effect of electrolytically occluded hydrogen on the magnetic properties of iron was due to the cold work produced in the metal by the process of occlusion.   Recrystallization was necessary fully to restore the magnetic properties.   Ewing[92] made

measurements on an annealed iron wire and on the same wire after 10 per cent extension in a testing machine and obtained the following:

Property	Annealed wire	Stretched wire
Maximum permeability.............	3080	670
Intensity of magnetization at $H = 40$	1230	1100
Residual induction, gausses..........	930	400
Coercive force, oersteds.............	1.7	4.5

The effect of cold rolling of several commercial irons and steels was investigated by Goerens.[240] His data for a basic Bessemer steel with 0.07 per cent carbon and 0.65 per cent total reported impurities are given in Table 49.

TABLE 49.—EFFECT OF COLD ROLLING ON MAGNETIC PROPERTIES OF LOW-CARBON STEEL*

Reduction in area, per cent	Maximum permeability	Maximum magnetizing force, oersteds	Residual induction, gausses	Coercive force, oersteds	Hysteresis loss, ergs per cu. cm. per cycle
None	1091	178	8200	3.5	24,400
41.6	442	180	6600	7.0	43,950
70.5	....	178.8	7900	10.1	
79.5	....	179.8	7600	11.0	
85.7	420	179.9	8000	12.7	75,200
89.2	415	179.0	9300	11.9	76,000
93.2	400	178.8	9200	13.0	77,200
95.2	410	178.4	9500	12.9	77,000
96.5	380	178.0	9800	14.8	78,650

* Goerens.[240]

The effect of cold rolling, for reductions between 8.83 and 75 per cent of the cross section, on the hysteresis loss of annealed polycrystalline and single-crystal specimens of electrolytic iron was determined by Gries and Esser.[831] Their results are shown in Figs. 53 and 54.
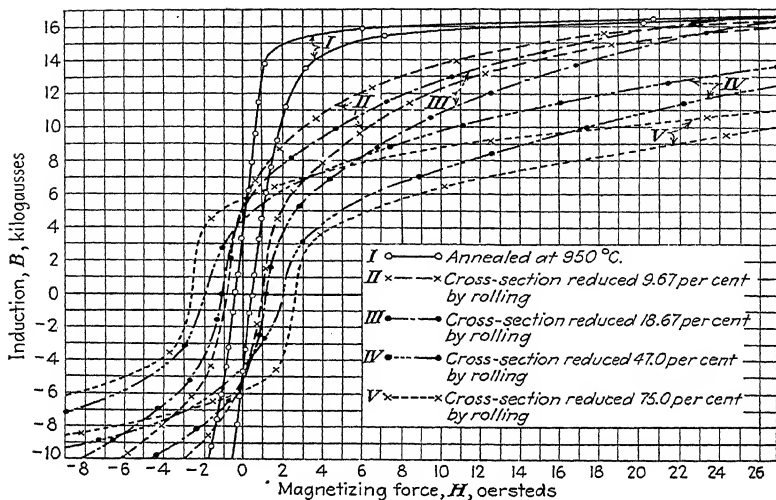
FIG. 53.—Effect of cold work on the hysteresis loop of polycrystalline electrolytic iron. *(Gries and Esser.*[831]*)*
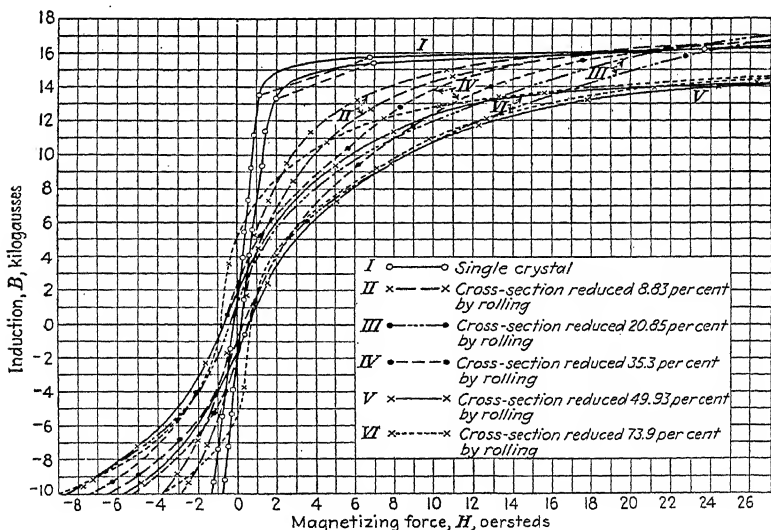
FIG. 54.—Effect of cold work on the hysteresis loop of an iron single crystal. *(Gries and Esser.*[831]*)*

The available data indicate that cold working decreases permeability and increases residual induction, coercive force, and hysteresis loss. Only the saturation intensity is unaffected by mechanical deformation.

130. Effect of Heat Treatment.—In considering the effect of annealing on the magnetic properties of iron and the deter-
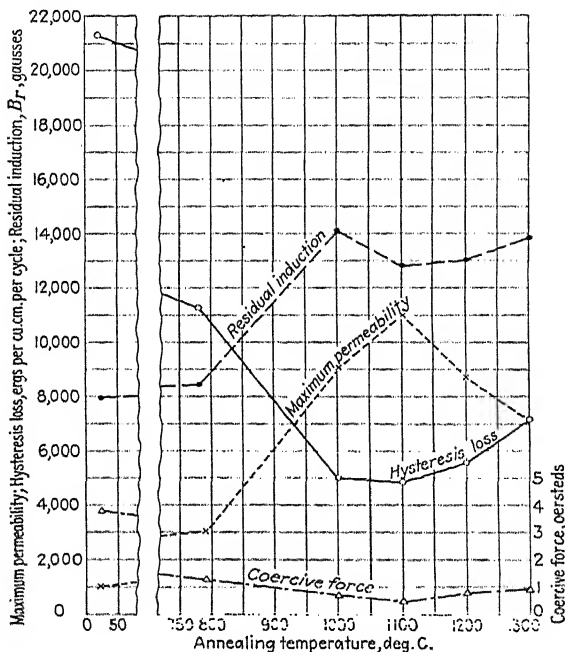
Fig. 55.—Effect of annealing on the magnetic characteristics of electrolytic iron. (*Terry.*[226])

mination of the optimum annealing temperature, it might be thought necessary to distinguish between the annealing of previously melted iron and of electrolytic iron as deposited, inasmuch as the removal of occluded hydrogen is an important factor in the annealing of electrolytic iron but is not involved in the case of fused iron. A survey of the data indicates, however, that the annealing temperature necessary to obtain the best magnetic properties is the same for both types of iron.

The data of Terry[225] for the hysteresis constants of Burgess' electrolytic iron, as deposited and annealed at temperatures up to 1300°C. (2370°F.), are reproduced in Fig. 55. The best results were obtained by annealing at 1100°C. (2010°F.). The maximum induction was not affected by changes in temperature.
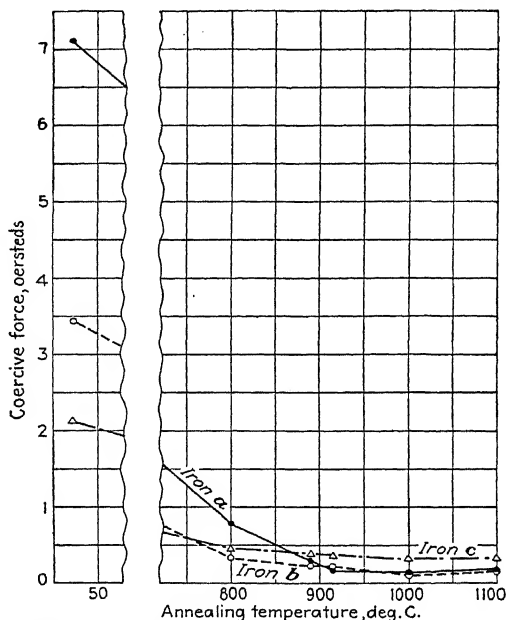
Fig. 56.—Effect of annealing on the coercive force of electrolytic iron. (*Gumlich.*[434])

The results reported by Burgess and Aston[208] for electrolytic iron before and after annealing were:

	For $H_{max.}$ = 200	
Treatment	Coercive force, oersteds	Residual induction, gausses
As deposited......................	18.5	11,200
Annealed at 675°C. (1245°F.).........	9.3	12,900
Annealed at 1000°C. (1830°F.).......	6.2	4,900
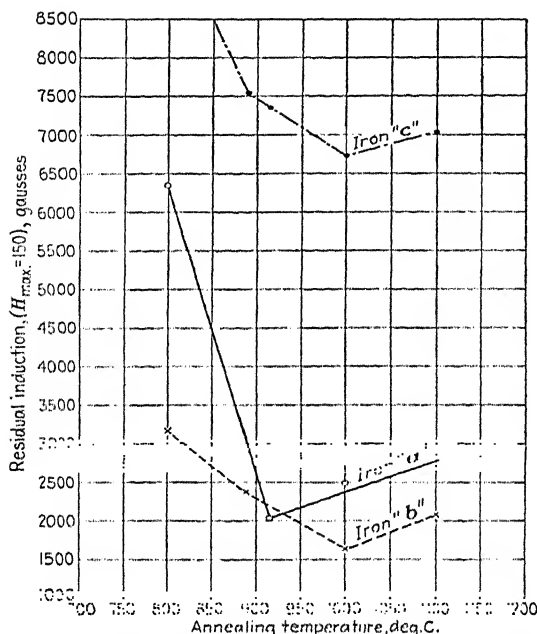
Fig. 57.—Effect of annealing on residual induction of electrolytic iron.
(*Gumlich.*[434])

The effects of annealing on the magnetic properties of Fischer electrolytic iron (as deposited) were reported by Gumlich[387] as follows:

Treatment	Coercive force, oersteds	Residual induction, gausses	Maximum permeability
Before annealing.....................	2.83	11,450	1,850
Annealed 24 hr. at 800°C. (1470°F.) and cooled slowly......................	0.375	10,850	14,400
Five heatings to 920°C. (1690°F.) with quick cooling......................	0.225	5,000	11,600
Thirteen heatings to 830°C. (1525°F.) with quick cooling.................	0.155	850	4,800

Results from a later investigation by Gumlich[434] are given in Table 50 and in Figs. 56 and 57.

TABLE 50.—EFFECT OF ANNEALING ON MAGNETIC PROPERTIES OF
ELECTROLYTIC IRON*

Annealing temperature		Induction, gausses, for $H = 150$			Coercive force, oersteds, for $H = 150$			Residual induction, gausses, for $H = 150$		
°C.	°F.	A†	B†	C†	A	B	C	A	B	C
As received		18,820	......	......	7.1	3.43	2.12	13,440		
800	1470	18,410	18,870	18,480	0.79	0.34	0.45	6,360	3,170	9,100
890	1635	17,950	18,740	18,530	0.30	0.235	0.395	2,920	2,380	7,550
915	1680	18,050	18,650	18,500	0.165	0.225	0.37	2,030	2,040	7,360
1000	1830	17,530	17,530	18,180	0.14	0.115	0.335	2,490	1,640	6,730
1100	2010	18,060	18,280	18,340	0.175	0.16	0.34	2,660	2,090	7,040

* Gumlich.[434]
† A = Griesheim electrolytic iron, as deposited.
  B = Fischer electrolytic iron, as deposited.
  C = Pfanhauser electrolytic iron, vacuum melted.

From data obtained on vacuum-melted electrolytic iron, Yensen[321] found that the permeability increased slowly with increasing temperature of annealing up to 700°C. (1290°F.), and then increased rapidly as the annealing temperature was raised from 700 to 800°C. Above 900°C. (1650°F.) the effect was uncertain. The permeability for low values of H decreased upon annealing at 950°C. (1740°F.) but rose again upon annealing at 1000°C. (1830°F.). For values of $H = 8$ or more, annealing at temperatures above 900°C. decreased the permeability.

In the course of his work with hydrogen-treated irons, Cioffi* found that high permeability was obtained when the treatment at high temperatures was followed by an anneal at a temperature not far below the A_3 point, for example at about 880°C. (1615°F.). The object of this anneal is to remove the strains introduced by lattice distortion during the transformation from gamma to alpha iron. Slow cooling through the transformation range is equivalent to a certain amount of subsequent annealing below the A_3 point. The importance of this annealing treatment, at temperatures below the A_3 point, had not been previously recognized and perhaps accounts for some of the inconsistent results which have been obtained from treatment at higher temperatures. The question will be treated more fully in a paper now in preparation in Dr. Cioffi's laboratory.

* Private communications.

F. MECHANOMAGNETIC EFFECTS

When a specimen of iron is magnetized, changes in length and volume occur; tension, pressure, or torsion therefore affects the magnetism of iron. The literature concerning these mechanomagnetic effects is voluminous, the interest in the phenomena being due largely to the possibility that light may be shed on the nature and mechanism of magnetism; their technological importance, however, is slight. These subjects belong in the realm of theoretical rather than practical magnetism, hence their present consideration is limited.

131. Effect of Tension.—The effect of tension on the magnetic properties of soft iron was investigated in 1885 by Ewing.[334] He found that, with constant field, the magnetization increased with increasing load until a maximum effect was reached at about 29,600 lb. per sq. in. Further increases in load decreased the effect on the magnetization. A reverse effect was observed during unloading but hysteresis evidently occurred. The maximum effect during unloading was ⋅ obtained at about 20,800 lb. per sq. in. With repeated loading and unloading the hysteresis decreased in amount but never disappeared completely. A more thorough study of the effect of tension was made by Honda and Terada,[1574] who found that it had no appreciable effect on the intensity of magnetization of Swedish iron for field strengths of about 24 oersteds; with lower field strengths the intensity of magnetization increased with increasing tension, and with field strengths greater than 24 oersteds the intensity decreased with increasing tension. Honda and Terada concluded that this effect was related to the phenomenon of magnetostriction.

Superimposition of an alternating current upon the magnetizing field eliminated hysteresis and increased the effect of tension on the magnetic properties, according to results obtained by McCorkle.[6234] In his experiments with a weak field (0.85 oersted) the maximum effect was obtained under a tension of about 145 lb. per sq. in.

Data which were obtained by Fischer* illustrate the effect of a tensile load on the intrinsic induction of electrolytic iron and of Armco iron. The electrolytic iron contained 0.016 per cent

* Unpublished data of M. F. Fischer, National Bureau of Standards.

carbon, 0.005 per cent phosphorus, 0.002 per cent sulphur, 0.001 per cent silicon, and less than 0.001 per cent manganese. Both irons were annealed at 950°C. (1740°F.) prior to test. The intrinsic induction for different field strengths was determined for the electrolytic iron both in the annealed condition and under a tension of 4750 lb. per sq. in., and for the Armco iron in the annealed condition and under a tension of 3564 lb. per sq. in. The differences between pairs of determinations, on loaded and unloaded specimens, are plotted in Fig. 58; a positive difference shows that the induction of the loaded specimen was greater
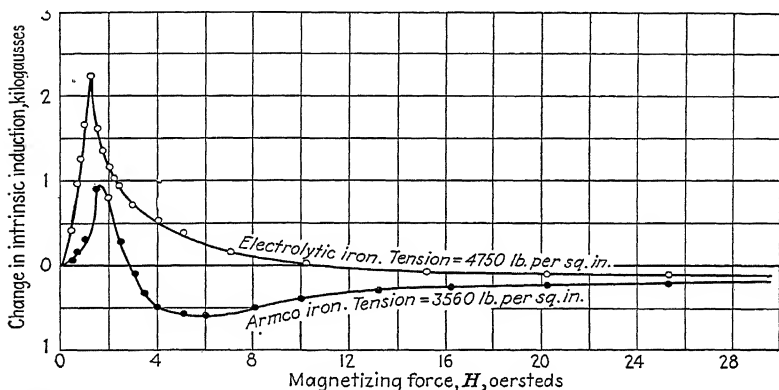
Fig. 58.—Effect of tension on the intrinsic induction of electrolytic iron and Armco iron. (*Unpublished data by Fischer.*)

than that of the unloaded specimen, at that particular field strength. Under these conditions the maximum effect of tension occurred at field strengths between 1 and 2 oersteds. The Villari point (no effect of tension) occurred at field strengths of 11 oersteds for electrolytic iron and less than 3 oersteds for Armco iron. The two curves are not directly comparable as the amounts of tension were different in the two cases.

The effect of tension on the magnetic properties of single crystals of iron was investigated by Webster.[640] Tension applied in the direction of the [1 0 0] axis increased the intensity of magnetization in all fields. The increase reached a maximum at a field strength of about 100 oersteds, then decreased with increasing field strengths to a value which was constant for field

strengths greater than 200 oersteds. Application of tension in the direction of the [1 1 0] axis caused an increase in magnetic intensity for field strengths of less than 125 oersteds but caused a decrease for fields of higher strength. Tension in the direction of the [1 1 1] axis caused a decrease in magnetic intensity for all field strengths.

The change in the magnetic properties which is caused by tension was used by Fraichet[507A,507B] and by Lopuchin[1062] as a means of accurate determination of the elastic limit of iron.

132. Effect of Pressure.—The effect of pressure on the magnetization of iron was investigated by Tomlinson,[40] Nagaoka and Honda,[81,95,111] Frisbie,[123] and Yeh.[589] The last determined the pressure effect for both electrolytic iron and steel and concluded that:

1. Within the range of pressure from 0 to 1200 kg. per sq. cm. at constant H, the relation between magnetization and pressure was linear.

2. Within the field range 0 to 100 gausses, the pressure coefficient per unit volume was negative.

3. At room temperature the percentage change of magnetization per unit volume was a maximum of -5.5 per cent per 1000 kg. per sq. cm. at $H = 1.2$ oersteds. The percentage change decreased rapidly on both sides of this maximum approaching the axis asymptotically for large values of H.

4. The absolute value of the pressure coefficient of magnetization per unit volume was less at high than at low temperatures.

5. The percentage change of magnetization with pressure was a very sensitive function of the carbon content.

6. The retentivity of iron decreased under pressure.

The temperature and pressure coefficients obtained by Yeh on electrolytic iron stated to contain 0.02 per cent of impurities are given in Table 51.

133. Volume Effects.—There have been many investigations of the change in volume or length of iron, with magnetization, but only a few representative investigations are reviewed here.

Nagaoka and Honda[81] found slight increase in the volume of an ovoid of Swedish iron when magnetized. Their data are given in Table 52.

134. Change in Length (Magnetostriction).—Schulze[805] made precise measurements of the magnetostriction (change in length) of electrolytic iron, commercial iron, steel, cast iron, and iron-nickel, iron-silicon, iron-aluminum, and iron-manganese alloys.

TABLE 51.—TEMPERATURE AND PRESSURE COEFFICIENTS OF MAGNETIZATION OF IRON*

Field strength, oersteds	Pressure coefficient $\Delta B/B$ per 1000 kg. per sq. cm.		Temperature coefficient $\Delta B/B$ per °C. at pressure P	
	At 25°C.	At 100°C.	$P = 0$	$P = 7050$ kg. per sq. cm.
0.43	−3.25	−0.99	+0.147	+0.177
0.61	−3.93	−2.09	0.171	0.195
0.86	−4.80	−3.69	0.232	0.247
1.08	−5.48	−4.87	0.285	0.294
1.30	−5.51	−5.39	0.263	0.264
1.51	−4.97	−4.65	0.153	0.158
1.73	−4.36	−3.70	0.126	0.135
1.94	−3.79	−3.08	0.097	0.106
2.16	−3.14	−2.61	0.072	0.079
4.32	−1.20	−1.23		

* Yeh.[589]

His results for electrolytic iron are shown in Fig. 59; his data for electrolytic iron and two commercial irons are given in Table 53. With increasing field strength electrolytic iron first increased rapidly in length to a maximum for a field strength of about

TABLE 52.—VOLUME CHANGE OF IRON WITH MAGNETIZATION*

Field intensity, H, oersteds	Intensity of magnetization, I	Volume change, $\Delta V/V$
2	155	$+0.1 \times 10^{-7}$
3	340	0.3×10^{-7}
4	540	0.4×10^{-7}
6	800	0.6×10^{-7}
12	1100	0.9×10^{-7}
17	1200	1.1×10^{-7}
29	1270	1.3×10^{-7}
49	1340	1.6×10^{-7}
113	1470	1.7×10^{-7}
151	1510	1.8×10^{-7}
203	1560	2.0×10^{-7}
251	1630	1.1×10^{-7}

* Nagaoka and Honda.[81]

50 oersteds, then shortened slowly, reached the Villari point (original length) at about 225 oersteds, and continued to contract in stronger fields. The most noticeable effect of impurities was to decrease the rate of contraction thus increasing the field strength necessary for the Villari point. The maximum increase in length for rapidly cooled electrolytic iron was greater (6.21×10^{-6} at $H = 56.4$ oersteds) than for slowly cooled iron, but the Villari point was unchanged.
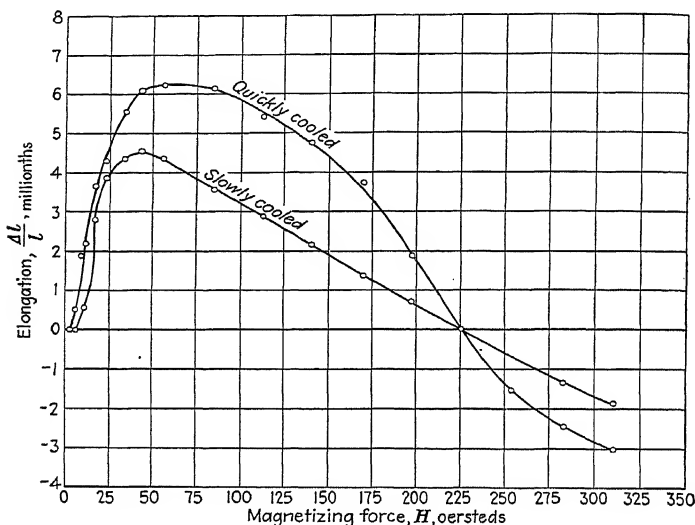
Fig. 59.—Magnetostriction of electrolytic iron. (*Schulze.*[805])

The magnetostriction of a series of steels with carbon contents between 0.058 and 1.37 per cent was determined by Dorsey,[210] the field strength being carried to much higher values than were used by Schulze. The purest specimen used by Dorsey (reported impurities, 0.137 per cent) had a maximum increase in length per unit length of 3.45×10^{-6} at $H = 40$ oersteds. At $H = 1580$ oersteds the contraction was 8.05×10^{-6}. The Villari point occurred at about $H = 230$ oersteds.

The influence of temperature on magnetostriction was investigated by Honda and Shimizu,[116] as shown in Fig. 60. Benedicks[297] investigated the magnetostriction of iron which con-

TABLE 53.—MAGNETOSTRICTION OF IRON*

Field strength, H, oersteds	$\frac{\Delta l}{l}$, millionths		
	Electrolytic iron	Iron, 99.7 per cent	Iron, 98.6 per cent
5.6	0.00		
11.3	+0.58	+1.44	+1.44
16.9	2.80		
22.6	3.87	3.66	3.50
33.8	4.36	4.94	4.73
45.1	4.40	5.31	5.14
56.4	4.36	5.18	5.18
67.7	......	4.94	4.98
84.6	3.58		
90.2	......	4.40	4.90
112.8	2.88	3.91	4.69
141.0	2.14	3.29	4.40
169.2	1.36	2.67	4.03
191.8	0.70		
225.6	0.00	1.36	3.09
282.0	−1.32	0.00	2.18
310.2	−1.89		
338.4	......	−1.19	1.44
372.2	......	......	0.82
406.1	......	......	0.29
439.9	......	......	−0.37

* Schulze.[805]

tained 0.008 per cent carbon, 0.009 per cent manganese, 0.014 per cent silicon, a trace of sulphur, and 0.002 per cent phosphorus. He found that with increasing temperature above 400°C. (750°F.) the magnetostriction increased rapidly to a maximum at about 500 to 550°C. (930 to 1020°F.), after which it decreased towards the temperature of the disappearance of ferromagnetism. Single crystals of iron not of high purity were investigated by Heaps,[513] Webster,[640] and Honda and Mashiyama.[669] Heaps noted that the magnetostriction varied with different crystal directions. Webster found that with fields up to $H = 600$ oersteds there was a continuing expansion for the tetragonal [1 0 0] axis, much greater than the maximum found in polycrystalline iron; for the trigonal [1 1 1] axis there was a continuing decrease in length, while for the digonal [1 1 0] axis there was increase in length
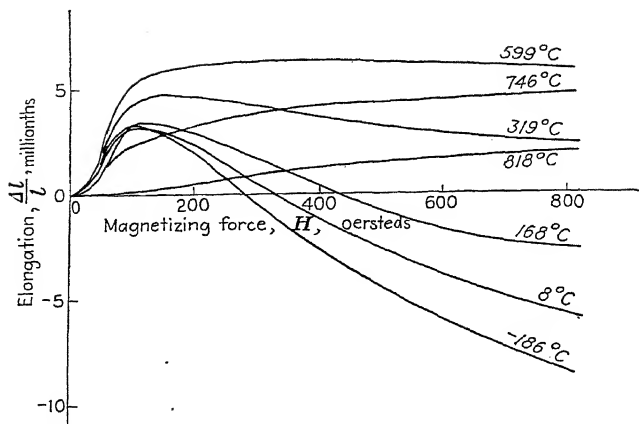
FIG. 60.—Magnetostriction of soft iron at various temperatures.   (*Honda and Shimizu.*[116])
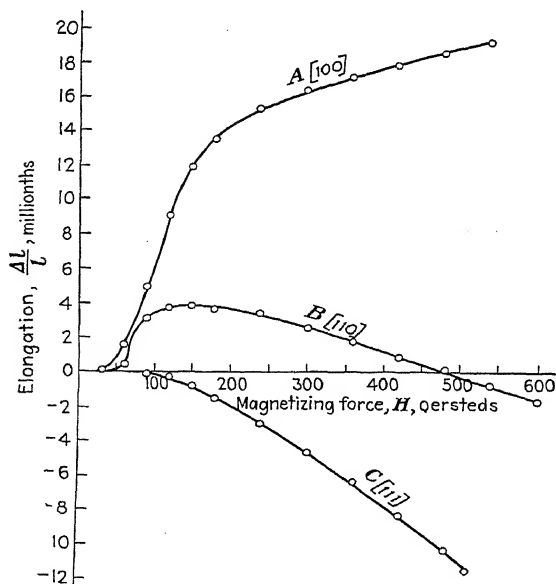
FIG. 61.—Magnetostriction of an iron single crystal.   (*Webster.*[640])

for weak fields followed by a decrease in length when magnetic saturation was approached. These results are shown in Fig. 61. The results on polycrystalline iron were a combination of the effects obtained for single crystals. The results of Honda and Mashiyama confirmed those of Webster. Akulov[756] derived values for the magnetostriction of single crystals of iron from theoretical considerations. These derived values were in agreement with the experimental results of Honda and Mashiyama.

The phenomenon of magnetostriction has greater practical importance than the other mechanomagnetic effects as it is believed to be responsible for noise in electrical transformers and in loud speakers.

G. GALVANOMAGNETIC AND THERMOMAGNETIC EFFECTS

The various galvanomagnetic and thermomagnetic effects, like the mechanomagnetic effects, are without practical application, whatever their importance may be in the field of theoretical magnetism.

If a plate of iron through which a current of electricity is passing is placed in a magnetic field so that the lines of magnetic force are at right angles to the plane of the plate and to the direction of flow of the current, one longitudinal and two transverse effects may be observed:

1. A transverse galvanomagnetic potential difference, or a rotation of the equipotential lines, the Hall effect.

2. A longitudinal galvanomagnetic potential difference, therefore, a change in electric resistance of the iron, sometimes called the Thompson effect.

3. A transverse galvanomagnetic temperature difference, the Ettinghausen effect.

If, instead of passing an electric current through an iron plate as for galvanomagnetic phenomena, a heat flow is established, that is, one end of the plate is kept at a higher temperature than the other, and the plate is placed in a magnetic field, four types of thermomagnetic phenomena may be observed:

1. A difference of potential on opposite sides of the plate, the Nernst effect.

2. A difference of potential at the ends of the plate.

3. A difference of temperature on the sides of the plate, the Righi-Leduc effect.

4. A change in the thermal conductivity of the iron.

135. The Hall Effect.—In the Hall effect, the transverse potential difference E is expressed by the equation:

$$-E = R\,\frac{HI}{d},$$

where R is the Hall coefficient, H the field strength, I the current in amperes, and d the thickness of the plate. Values for the Hall coefficient as determined by Smith[223] for Kahlbaum iron and by Alterthum[251] for Kahlbaum electrolytic iron are given in Table 54. Frey[329] determined the Hall effect in transformer plate.

TABLE 54.—THE HALL EFFECT IN IRON

Temperature, °C.	Hall coefficient, R, thousandths	
	Smith[223] for $H = 17,000$	Alterthum[251] for $H = 6,900$
−253	. . . . . .	1.99
−190	0.75	1.87
− 79	. . . . . .	5.25
+ 18	. . . . . .	11.90
22	11.0	
100	18.9	
184	29.2	
300	50.4	
545	167	
654	243	
735	319	
796	120	
835	32.8	
900	9.0	

136. The Thompson and Ettinghausen Effects.—The increase in the electric resistance of iron when magnetized longitudinally is sometimes called the Thompson effect as it was first observed by Thompson,[10] in 1856. Heising[305] found that this increase in resistance in longitudinal fields was slightly greater for electrolytic iron than for ordinary soft iron. In transverse fields the resistance decreased with increasing field strength. Heaps[241] and others reported an initial increase in resistance in weak

transverse fields with a reversal and subsequent decreasing resistance with continued increase in field strength. The recent work of Stierstadt[945] with electrolytic iron of high purity confirmed Heising's observation of a continual decrease in transverse fields. Stierstadt[908] found that the change in resistance in longitudinal fields might be twice as great for electrolytic iron as for ordinary iron, and that the previous
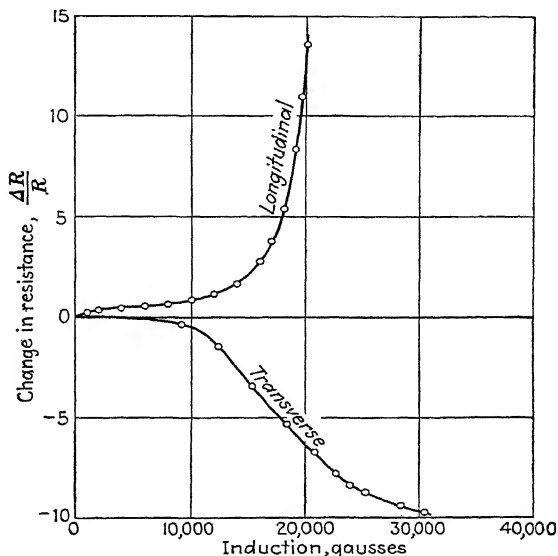
Fig. 62.—Change in electric resistance of electrolytic iron in longitudinal and transverse fields. (*Stierstadt.*[945,983])

thermal and mechanical treatments affected the amount of the change to a marked extent. In transverse fields, however, electrolytic iron showed less change in resistance than did iron containing impurities. The change in resistance of electrolytic iron in longitudinal and transverse fields is shown in Fig. 62.

Webster[695,749] worked with single crystals of iron and found that in longitudinal fields there was no change along the [1 1 0] axis; for the [1 1 1] axis there was no change until a magnetic intensity of about 800 c.g.s. units was reached, the resistance thereafter increased with increasing field until magnetic saturation

was approached when the value $\Delta R/R$ tended to a limiting value of 0.40 per cent. For the [1 1 0] axis the change was similar to the [1 1 1] axis but with the limiting value of $\Delta R/R$ about 0.28 per cent. In transverse fields there was always a gradual decrease in resistance for field strengths below 5000 gausses and above 12,000 gausses, but in the region between these two values there occurred a rapid change of resistance which was positive when the current was along a cubic axis but negative for the other two directions.

The influence of temperature on the change in resistance in magnetic fields was investigated by Williams[137] who found that the change diminished with increasing temperature; the temperature effect was more noticeable at high field intensities than at low.

In the Ettinghausen effect the transverse temperature difference (ΔT) is expressed by the formula:

$$\Delta T = P\frac{HI}{d}$$

where H is the field strength in oersteds, I is the current in amperes flowing through the plate, d is the thickness of the plate in centimeters, and P is the Ettinghausen coefficient.

Values for the Ettinghausen coefficient, reported by Zahn[127,138] and by Hall and Campbell,[213] are given in Table 55.

TABLE 55.—ETTINGHAUSEN COEFFICIENT OF IRON

Material	Temperature, °C.	Field strength, oersteds	Ettinghausen coefficient, P	Investigator
Electrolytic iron.......	18	6290	-0.57×10^{-7}	Zahn[127]
Steel........	20	....	-0.67×10^{-7}	Zahn[138]
Soft iron.....	12.2	5000	-0.492×10^{-7}	Hall and Campbell[213]
Soft iron.....	83.9	5000	-0.612×10^{-7}	Hall and Campbell[213]

A longitudinal galvanomagnetic temperature difference, having the same relation to the Ettinghausen effect as the Thompson effect has to the Hall effect, has been observed for certain other metals, but Hall and Campbell[213] were unable to detect any longitudinal galvanomagnetic temperature effect in soft iron.

137. The Nernst Effect.—The potential difference E of the Nernst effect may be expressed by the equation

$$E = QHw\frac{dt}{dl}$$

where Q is the Nernst coefficient, H is the field strength, w is the width of the plate, and dt/dl the temperature gradient per unit length. Table 56 contains values found in the literature for the Nernst coefficient for iron.

TABLE 56.—NERNST COEFFICIENT FOR IRON

Material	Temperature, °C.	Field strength, oersteds	Nernst coefficient, Q, thousandths	Investigator
Wrought iron...	.....	626	−1.62	Nernst[37]
Wrought iron...	.....	1,620	−1.5	Nernst[37]
Soft iron.......	48	10,800	−0.87	Campbell[503]
Electrolytic iron	55	6,290	−1.05	Zahn[127]
Soft iron.......	31	5,550	−0.86	Hall and Campbell[213]
Soft iron.......	60	5,550	−0.98	Hall and Campbell[213]
Electrolytic iron	55	......	−0.975	Smith[448]
Iron...........	48.6	2,100	−1.0	Unwin[296]
Iron...........	48.6	22,650	−0.91	Unwin[296]
Iron...........	129.2	2,000	−1.09	Unwin[296]
Iron...........	129.2	22,100	−0.86	Unwin[296]
Steel..........	.....	880	−0.627	Nernst[37]
Steel..........	.....	2,960	−0.702	Nernst[37]
Steel..........	.....	......	−1.66	Zahn[138]

In addition to the potential difference found between the sides of a plate through which heat is flowing, when placed in a magnetic field, there is also a potential difference between the ends of the plate. This longitudinal potential difference E is expressed by the equation:

$$E = LH^2d\frac{dt}{dl}$$

where L is the coefficient of the effect, H the field strength, d the distance between the two points across which the potential is measured, and dt/dl the temperature gradient per unit length.

Hall and Campbell[213] measured the effect on soft iron at 47°C. (117°F.) and obtained the following values for L:

Field strength, H, oersteds.	2,000	,200	12,000
Coefficient, L, thousandths.	2.11	0.83	0.80

138. The Righi-Leduc Effect.—This effect is observed when an iron plate through which heat is passing is placed in a magnetic field with the field at right angles to the plane of the plate and the flow of heat. A temperature difference is observed between points on the opposite sides of the plate, which were isothermal before introduction into the magnetic field. The temperature difference, Δt, is expressed by the formula

$$\Delta t = SHw\frac{dt}{dl}$$

where S is the Righi-Leduc coefficient, H the field strength, w the width of the plate, and dt/dl the longitudinal temperature gradient per unit length. Values which have been reported for the Righi-Leduc coefficient of iron are given in Table 57.

TABLE 57.—RIGHI-LEDUC COEFFICIENT FOR IRON

Material	Temperature, °C.	Field strength, oersteds	Righi-Leduc coefficient, S, millionths	Investigator
Soft iron	30.6	5,600	+0.568	Hall and Campbell[213]
Soft iron	60.2	5,500	0.632	Hall and Campbell[213]
Soft iron	48	7,300	0.608	Campbell[503]
Electrolytic iron	56.9	11,900	0.392	Smith and Smith[338]
Electrolytic iron	....	6,290	0.39	Zahn[127]
Iron	....	......	0.52	Unwin[296]
Steel	....	......	0.687	Zahn[138]

Under the same conditions in which the Righi-Leduc effect is observed, there will also be found a change in temperature difference between the two ends of the plate, in other words, the thermal conductivity of iron changes upon magnetization. This change was investigated by Battelli,[34] Korda,[88] Schweit-

zer,[98] Blyth,[113] Lafay,[117] Hall and Campbell,[213] and Brown.[769] The most recent work, that of Brown, showed a decrease of 1.14 per cent in the thermal conductivity of iron when placed in a longitudinal field of 10,000 oersteds. In a transverse field there was a decrease of 0.4 per cent for 4000 oersteds field strength, but no measurable change in a field of 8000 oersteds.
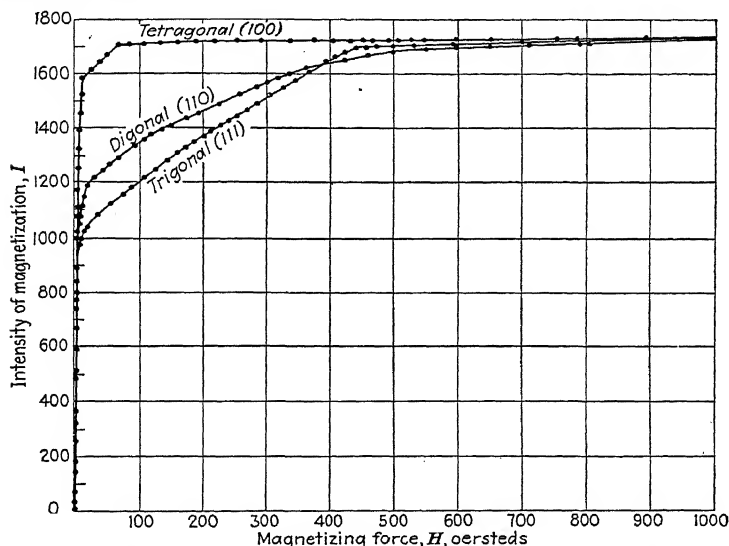
FIG. 63.—Magnetization curves in the (1 1 0) plane of an iron single crystal. (*Honda and Kaya.*[667])

H. MAGNETIC PROPERTIES OF SINGLE CRYSTALS OF IRON

The factors which exert the most important effects on the magnetic properties of iron are those which affect the substance rather than the crystalline aggregate which constitutes the material. The importance of grain size, in the range of sizes ordinarily encountered in polycrystalline material, indicates the necessity for determinations of the properties of single crystals, to obtain information in regard to the fundamental magnetic properties of iron. The ultimate results of course will be obtained from single-crystal specimens of absolutely pure iron, when such specimens are available. The magnetic properties

of single iron crystals were investigated by Beck,[834] Webster,[639] Honda and Kaya,[667] Honda, Kaya, and Masuyama,[668] Honda, Masumoto, and Kaya,[783] Gerlach,[612,663,664,883,884] Dussler and Gerlach,[706] Dussler,[771] Gries and Esser,[831] Sizoo,[860] and Kaya.[1009]

Impure iron was used in the investigations of Beck, Webster, and Honda and his coworkers. Their results, although not directly applicable to pure iron, nevertheless are of value in regard to the magnetic characteristics of single crystals. Figure 63 shows the results of Honda and Kaya[667] for the difference in magnetic effects in a single plane of a crystal when the measurements were made in the direction of different axes which lie within the plane. Gerlach[663] found that the hysteresis loss of single crystals of electrolytic iron was very low as compared with that of the same iron in the polycrystalline state. The magnetization curve was a straight line up to 13,000 gausses ($H = 5$ oersteds). After a sharp bend the curve had the usual form of this type of curve. Table 58 shows Gerlach's results for the residual induction of single-crystal and polycrystalline electrolytic iron.

TABLE 58.—RESIDUAL INDUCTION OF ELECTROLYTIC IRON*

Magnetizing field, oersteds	(Relative) residual induction, gausses	
	Single crystal	Polycrystals
2.5	5	12
5	7	25
10	8	41
20	9	53
50	10	74
150	10	125
250	6	130
380	4	130

* Gerlach.[663]

The results of Gerlach[884] indicated to him that, as was suggested by Yensen[590] at an earlier date, coercive force and hysteresis loss would be zero in a single crystal of iron which was chemically pure and free from internal tension. However, measurements

by Sizoo[860] on single crystals of high-purity iron showed that there was no increase in the size of the hysteresis loop for field strengths greater than about 15 oersteds and that the residual induction was the same as that of polycrystalline iron. According to Kaya[1009] the retentivity of single crystals of iron is given by the expression $\frac{I_\infty}{l + m + n}$, where I_∞ is the saturation value of magnetization and l, m, and n are the direction cosines of the external fields as related to the cubical axes, or to their spacial coordinates. Hill[971] found that the magnetization curve of single iron crystals was linear for field strengths of less than 2.0 oersteds, with no magnetic lag. The magnetization curve for fields up to 20 oersteds was non-linear except for the initial stage. The hysteresis loss which was present for field strengths between 2 and 20 oersteds increased with decrease in temperature. Ruder[1071] reported that the hysteresis loss of a single crystal of iron varied as much as 2:1 depending upon the orientation.

Dussler and Gerlach[706] found that the saturation intensity for a single crystal of iron was 1710 ± 8, at a field strength of between 600 and 800 oersteds for the digonal axes, and at 150 oersteds for the tetragonal direction. The field strength for saturation in the tetragonal direction was:

Temperature, °C................	20	629	680	739
H, oersteds....................	150	4.5	3.5	2.5

The relation between saturation intensity and temperature for single crystals of iron with field parallel to the tetragonal axis was studied by Honda, Masumoto, and Kaya.[783] The value at absolute zero in the following data was obtained by extrapolation:

Temperature °C.	Absolute zero	−190	+5	107	215	300	400	500	600	700	750	770
Saturation intensity	1753	1741	1710	1679	1631	1590	1517	1409	1270	993	682	382

The magnetization of single crystals of iron between 20°C. (68°F.) and 755°C. (1390°F.) was investigated by Dussler.[771]
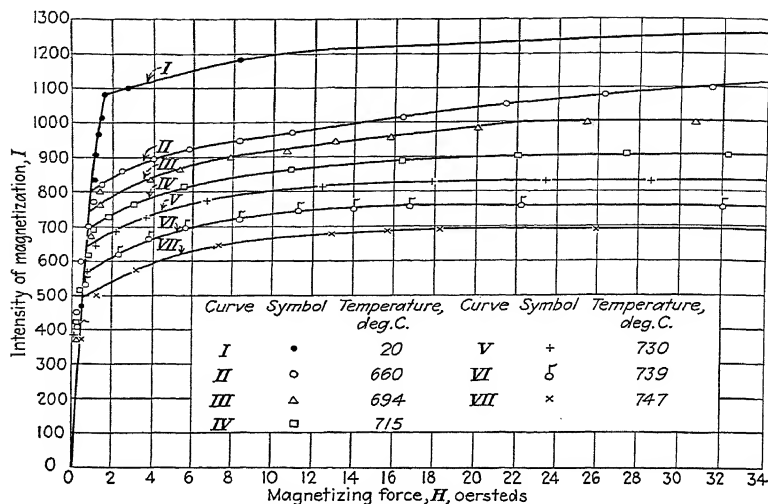
FIG. 64.—Magnetization curves, at various temperatures, in the (1 1 0) plane of an iron single crystal.   (*Dussler.*[(771)])
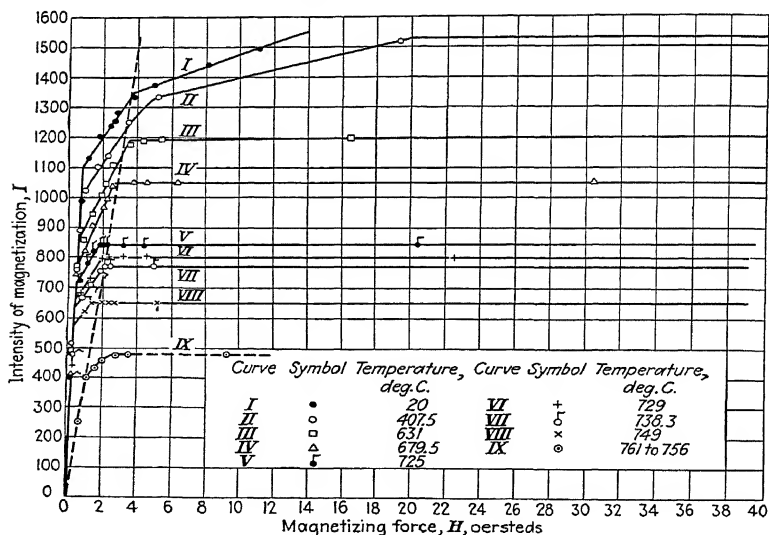
FIG. 65.—Magnetization curves, at various temperatures, in the (1 0 0) plane of an iron single crystal.   (*Dussler.*[(771)])

Some of his results are shown in Figs. 64 and 65. The saturation intensity decreased with rising temperature according to an exponential law and had about the same value for the digonal and the tetragonal axes but reached saturation in lower fields for the tetragonal direction. Following are the saturation intensities found:

Digonal axis

Temperature, °C	20	407	631	660	682	694	715	730	739	749
Saturation intensity	1709	1534	1200	1111	1068	1006	907	835	763	691

Tetragonal axis

Temperature, °C	20	403	409	631	679	723	729	735	740	747	756
Saturation intensity	1718	1560	1551	1200	1075	861	814	704	730	649	480

I. AUTHORS' SUMMARY

The magnetic properties of iron are so dependent upon the amount and type of impurities present and upon the previous mechanical and thermal history of the material that there does not seem to be justification for presenting any particular set of values as characteristic of high-purity iron. Furthermore our knowledge of the effects of small amounts of impurities is not sufficient to permit prophecy as to the magnetic properties of pure iron. The anomalous effect of impurities is illustrated by the fact that hydrogen-treated ingot iron has magnetic properties far superior to those of annealed electrolytic iron of greater purity. Yensen believes that the ferromagnetic property of iron is a function of (1) lattice distortion and (2) lattice orientation, and that all of the contributing causes such as impurities, grain size, or thermal and mechanical treatments, can be combined under the general heading "Causes of Lattice Distortion." Authorities on magnetic phenomena in iron quite generally agree that magnetic properties are properties of the substance rather than of the crystalline aggregates which comprise the material iron. Consequently the ultimate magnetic properties will be obtained in single-crystal specimens of absolutely pure metal. Opinions have been expressed that the coercive force

and hysteresis loss of a single crystal of absolutely pure iron would be zero and that the maximum permeability would be 500,000 or more. The confirmation of these hypotheses awaits the preparation of single crystals of absolute purity.

Up to the present time the magnetic properties of iron alloys have been more important for practical purposes than the properties of purified iron. The addition of substitutional elements such as nickel, cobalt, silicon, and manganese produces beneficial effects in iron alloys which can be duplicated in purified iron only by the removal of interstitial elements such as carbon, oxygen, nitrogen, and sulphur. The removal of these interstitial elements is a difficult process and has been attempted only on a laboratory scale. Future applications for magnetic purposes, of purified iron or of alloys made from purified iron, are subjects for interesting speculation.

CHAPTER VIII

MISCELLANEOUS PROPERTIES

Density—Compressibility—Optical Properties—Authors' Summary

In a review of existing information on the properties of high-purity iron, occasional references are encountered to what may be termed miscellaneous properties. The most important of these, density, compressibility, and optical properties, are summarized in this chapter.

A. DENSITY

Accurate knowledge of the density of a metal is of vital importance in matters of structural design, but a review of existing information shows clearly that the density of iron cannot be stated with the precision which would be desirable for so important a structural material. The density of a small sample can be determined with extreme precision, but the result applies only to that individual specimen, not to the material as a whole. For this reason some of the reported results of density determinations, in which five significant figures were given, have been rounded off in this review.

139. Direct Determinations of Density.—The earliest value reported for the density of electrolytic iron, 7.324 g. per cu. cm., as determined by Houllevigue[74] in 1897, is also the lowest value found for high-purity iron. A difficulty encountered by Houllevigue, the formation of bubbles of hydrogen on the iron by reaction with the water, probably accounts for the low density which he obtained. A more probable value, 7.875 g. per cu. cm., was reported by Hegg[214] in 1910 for melted electrolytic iron. Levin and Dornhecker[286] found that the density of unannealed electrolytic iron was 7.875 g. per cu. cm., and that annealing lowered it to 7.871. The density of electrolytic iron, containing 0.035 per cent of determined impurities, was reported by Gümlich[387] as 7.878 g. per cu. cm. A density of 7.90 was reported by Tritton and Hanson[585] for electrolytic

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iron containing 0.007 per cent phosphorus, 0.08 per cent oxygen, and traces of carbon, silicon, sulphur, and manganese. Austin and Pierce[1046] determined the density of four specimens of high-purity iron which were subsequently used in their investigation of the temperature of the A_3 transformation. They found that the density of vacuum-melted electrolytic iron was 7.864 g. per cu. cm. at 26.8°C. (80°F.); of powdered carbonyl iron melted in moist hydrogen, 7.848 g. per cu. cm. at 23.8°C. (75°F.); of some of the same powdered carbonyl iron sintered in moist hydrogen at 1500°C. (2730°F.) for 18 hr., 7.856 g. per cu. cm. at 25.2°C. (77°F.); and of a carbonyl-iron plate, 7.877 g. per cu. cm. at 24.1°C. (75°F.). The density of the latter plate was not affected by 47 hours' treatment in hydrogen at 1500°C.

The density of open-hearth ingot iron was reported by O'Neill[575] as 7.858 g. per cu. cm. at 20°C. (68°F.), by Ishigaki[671] as 7.868, and by Tamaru [863] as 7.887 g. per cu. cm. The results of Cross and Hill[703] for two electrolytic irons and two high-purity commercial irons were:

Sample No.	Material	Composition, per cent						Density at 20°C., g. per cu. cm.
		C	Mn	P	S	Si	Cr	
171	Vacuum-fused electrolytic iron, hot rolled.................	0.001	.....	.....	0.011	0.004	.....	7.869
914	Vacuum-fused electrolytic iron..	0.01	0.09	0.020	0.007	0.01	.....	7.867
F77	Pure commercial iron, annealed at 775°C. (1425°F.)...........	0.027	.....	.....	0.023	0.003	0.055	7.855
V1	Pure commercial iron, annealed at 900°C. (1650°F.)...........	0.017	.....	.....	.....	.....	.....	7.865
								Av. 7.864

Cross and Hill's value, 7.869, for their sample 171, was cited by Heindlhofer[556] and is credited to him in Abegg's Handbook.[914]

The density of commercial electrolytic iron was reported by Fuller[662] as 7.899 g. per cu. cm. Kaya[786] reported the density of a single crystal of iron as 7.870 g. per cu. cm., greater by 0.037 per cent than the density of the same iron in the poly-crystalline condition.

Selected values for the density at room temperature, determined by direct measurement, are given in Table 59.

Table 59.—Density of Iron at Room Temperature, by Direct Measurement

Investigator	Year	Density, g. per cu. cm.
Electrolytic iron		
Hegg[214]................	1910	7.875
Levin and Dornhecker[286]...	1914	7.871
Gumlich[387]..............	1918	7.875
Tritton and Hanson[585].....	1924	7.90
Cross and Hill[703]..........	1927	7.869
Cross and Hill[703]..........	1927	7.867
Austin and Pierce[1046]......	1934	7.864
		Av. 7.874
Carbonyl iron		
Austin and Pierce[1046]......	1934	7.848
Austin and Pierce[1046]......	1934	7.856
Austin and Pierce[1040]......	1934	7.877
		Av. 7.860
Ingot iron		
O'Neill[575]................	1924	7.858
Ishigaki[671]..............	1926	7.868
Cross and Hill[703]..........	1927	7.855
Cross and Hill[703]..........	1927	7.865
		Av. 7.861

140. Density by Extrapolation.—Several investigators have derived values for iron by extrapolating to zero content of alloying element the densities of a series of iron alloys. Values so obtained, for room temperature, are given in Table 60.

141. Density from Lattice Constant.—The density of a metal with body-centered cubic lattice can be calculated from the lattice constant a_0 by means of the following equation:

$$\text{Density} = \frac{2 \times \text{mass of atoms}}{(a_0 \times 10^{-8})^3}$$

For iron the density $\dfrac{2 \times 55.84 \times 1.65 \times 10^{-24}}{(a_0 \times 10^{-8})^3}$

TABLE 60.—DENSITY OF IRON BY EXTRAPOLATION

Investigator	Year	Density at room temperature, g. per cu. cm.
Benedicks[119]	1904	7.85
Gumlich[387]	1918	7.876
Andrew and Honeyman[541]	1924	7.864
Ishigaki[671]	1926	7.880

Av. 7.868

The lattice constants reported by several investigators have been used to obtain the values in Table 61 for the density of iron.

TABLE 61.—DENSITY OF IRON COMPUTED FROM THE LATTICE CONSTANT

Investigator	Year	Lattice constant, Å.	Density, g. per cu. cm.
Davey[551]	1924	2.861	869
Heindlhofer[566]	1924	2.864	844
Wever[587]	1924	2.863	852
Davey[602]	1925	2.855	918
Blake[595]	1925	.860	874
Brill and Mark[768]	1928	863	852
Eisenhut and Kaupp[773]	1928	863	852
Mayer[845]	1929	861	869
Esser and Müller[997]	1933	2.861	866

Av. 7.865

142. Density of Iron above 100°C.—The density of iron at elevated temperatures can be calculated by means of the linear coefficient of expansion β, assuming the volume coefficient to be three times the linear coefficient, by means of the equation

$$D_2 = \frac{D_1}{1 + 3\beta(t_2 - t_1)}$$

where D_2 and D_1 are the densities at temperatures t_2 and t_1, respectively. Using the thermal expansion data of Souder and Hidnert[490] and of Austin and Pierce,[1046] with 7.87 g. per cu. cm.

as the density of iron at 25°C., the following values are obtained for the density at elevated temperatures:

Temperature		Density, g. per cu. cm.
°C.	°F.	
100	210	7.85
200	390	7.82
300	570	7.78
400	750	7.74
500	930	7.71
600	1110	7.67
700	1290	7.63
800	1470	7.59

Values for the density of alpha, gamma, and delta iron have been calculated by Ralston* from the thermal-expansion data of Honda[370] and of Satô.[630] Ralston's values rounded to four significant figures, are:

Modification	Temperature		Density, g. per cu. cm.
	°C.	°F.	
Alpha......................	906	1663	7.571
Gamma.....................	906	1663	7.633
Gamma.....................	1400	2552	7.408
Delta......................	1400	2552	7.390
Delta......................	1535	2795	7.355

More precise values for the volume changes at the transformation points are necessary before densities derived from thermal-expansion data for temperatures above Ac_3 can be accepted as more than approximations.

Densities of alpha and delta iron can be derived from the lattice constants by means of the equation previously given.

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* Reference 853, pp. 172–182.

Substitution of the a_0 values of Westgren and Phragmén[493] in the equation give the following:

| Modification | Temperature | | Lattice constant, Å. | Density, g. per cu. cm. |
	°C.	°F.		
Alpha............	800 to 825	1472 to 1517	2.90	7.55
Delta............	1425	2597	2.93	7.32

143. Density of Molten Iron.—The values reported for the density of molten iron are given in Table 62. Ralston's value was calculated* from the thermal-expansion data of Satô[630] for solid iron and the data of Honda and Endo[721] for the volume change at the melting point.

TABLE 62.—DENSITY OF MOLTEN IRON

| Investigator | Year | Temperature | | Density, g. per cu. cm. |
		°C.	°F.	
Roberts and Wrightson[33]....	1883	m.p.		6.88
Benedicks, Berlin, and Phragmén[547]..................	1924	m.p.		6.92 ± 0.07
Berlin[652]..................	1926	1530	2785	7.45
Berlin[652]..................	1926	1530	2785	7.38
Berlin[652]..................	1926	1670	3040	6.95
Berlin[652]..................	1926	1670	3040	6.94
Ralston[853].................	1927	1535	2795	7.10
Benedicks, Ericsson, and Ericsson[817]..................	1930	1533	2790	7.23
Benedicks, Ericsson, and Ericsson[817]..................	1930	1600	2910	7.16

144. Summary of Density Data.—The averages of the selected values for the density of iron at room temperature by the three methods are:

Direct determination.................. 7.867 g. per cu. cm.
By extrapolation..................... 7.868 g. per cu. cm.
From lattice constant................. 7.865 g. per cu. cm.

Average.......... 7.867 g. per cu. cm.

* Reference 853, p. 178.

In view of the considerable range of values used in obtaining the above averages (7.847 to 7.93 g. per cu. cm.) a rounded value of 7.87 g. per cu. cm. is suggested as a probable value for the density of pure iron at room temperature.

Values for the density of iron at elevated temperatures are based upon thermal-expansion data and for temperatures above the A_3 point are unsatisfactory because of lack of reliable data for the volume changes at the transformation points.

Of the reported values for the density of molten iron those of Benedicks, Ericsson, and Ericson[817] seem to be the most probable.

B. COMPRESSIBILITY

The cubic compressibility of wrought iron was reported by Richards and Brink[165] as slightly more than 10 per cent of the compressibility of mercury. Subsequently, Richards[334] gave a corrected value of 0.60×10^{-6} per bar or 0.61×10^{-6} per atmosphere for the compressibility of iron at 20°C. between 100 and 500 bars pressure; the corrected value was based on a new calibration of his Bourdon gage and on a new determination, 3.95×10^{-6} per bar, of the compressibility of mercury. Grüneisen[176] calculated the cubic compressibility of iron, from elastic constants, as 0.62×10^{-12} in c.g.s. units or 0.63×10^{-6} per atmosphere at 18°C. He[212] also determined the compressibility of iron by the method of Malloch, measuring the deformation of a tube under internal pressure. The values obtained were:

Temperature, °C	−190	18	128	165
Compressibility, sq. cm. per kg. $\times 10^6$	0.606	0.633	0.664	0.675
Compressibility per atmosphere $\times 10^6$	0.626	0.654	0.686	0.698

The outstanding work on the compressibility of iron is that of Bridgman[463] on Armco iron. He determined the linear compressibility and from this calculated the cubic compressibility on the assumption that the linear compressibility is equal in all directions, a plausible assumption for a metal which crystallizes in the cubic system. Bridgman found that the change in volume produced by any pressure p, in the pressure range 0 to 12,000 kg. per sq. cm., could be expressed by the equations:

At 30°C. $\quad \dfrac{\Delta V}{V_0} = -0.587p \times 10^{-6} + 2.1p^2 \times 10^{-12}$

At 75°C. $\quad \dfrac{\Delta V}{V_0} = -0.593p \times 10^{-6} + 2.1p^2 \times 10^{-12}$

If p is expressed in normal atmospheres, the equations become

At 30°C. $\quad \dfrac{\Delta V}{V_0} = -0.606p \times 10^{-6} + 2.2p^2 \times 10^{-12}$

At 75°C. $\quad \dfrac{\Delta V}{V_0} = -0.613p \times 10^{-6} + 2.2p^2 \times 10^{-12}$

At 30°C. the mean compressibility between 0 and 10,000 kg. per sq. cm. was 0.566×10^{-6} per kilogram per square centimeter or 0.585×10^{-6} per atmosphere; at 75°C. over the same pressure range it was 0.572×10^{-6} per kilogram per square centimeter or 0.591×10^{-6} per atmosphere. The pressure coefficient of compressibility for the range of pressure used by Bridgman was 7.0×10^{-6} per kilogram per square centimeter or 7.2×10^{-6} per atmosphere. The temperature coefficient of compressibility calculated from the above equations was 2.3×10^{-4} per degree centigrade for the temperature range 30 to 75°C. Bridgman observed that increase in impurities increased the compressibility of iron.

Only one determination of the compressibility of a specimen of high-purity iron has been found. This was a comparison, by Adams,[*] of the compressibility of a specimen of Yensen iron with that of a specimen of Bessemer steel. The compressibilities of the two specimens, at pressures of 0 and 7000 kg., were almost identical (within 1 part in 500), which indicates that the compressibility of iron is not materially affected by an increase in purity.

C. OPTICAL PROPERTIES

Two of the optical properties of iron, reflectivity and emissivity, are important in the field of pyrometry. Reflectivity is the relation between the amount of radiant energy which is reflected from a surface and the amount of energy which was incident to the surface. Emissivity is a measure of the radiant energy of an

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[*] Private communications from Dr. L. H. Adams of the Geophysical Laboratory, Carnegie Institute of Washington, and from Dr. John Johnston of the Research Laboratory, United States Steel Corporation.

object in comparison with the radiant energy emitted by a black body at the same temperature.

145. Reflectivity.—Values for the reflectivity of iron have been reported by Rubens,[46] Rubens and Nichols,[77] Trowbridge,[83] and Coblentz.[233] Only Coblentz has given information regarding the composition of the material used, which he stated had an iron content of 99.8 per cent. Results from the four investigations are given in Fig. 66.
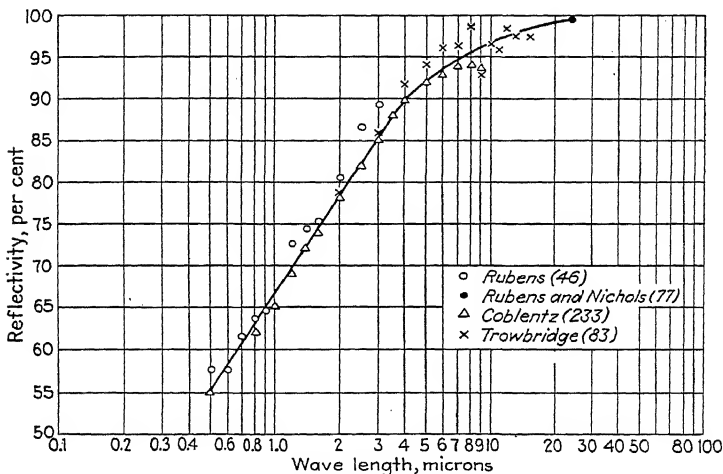
FIG. 66.—Reflectivity of iron.

146. Emissivity.—Emissivity is the ratio between the amounts of radiant energy emitted by an object, for example iron, at a particular temperature and by a black body at the same temperature. Emissivity corrections must be applied to all optical pyrometric observations on objects which do not conform strictly to the laws of black-body radiation, as the calibration of pyrometers is based on the black-body laws. Emissivity varies with different wave lengths of light, consequently corrections may be applied for total emissivity or for any one of a number of spectral emissivities. If a radiation pyrometer is used, a correction for total emissivity must be applied; for optical pyrometers a correction for the emissivity at an effective wave length of about 0.65μ ordinarily is used.

Relatively few determinations of the emissivity of high-purity iron have been reported. Bidwell[268,298] reported emissivity values of from 23 to 63 per cent, depending on the temperature, on what may have been originally a relatively pure iron. However, the source of heat was an arc between carbon electrodes; a carbon cup, for black-body measurements, floated on the surface of the liquid iron and a carbon rod remained in the iron during solidification to produce a hole for black-body measurements on the solid iron. It is quite certain that the measurements were made on an iron which was impure at least with respect to carbon. Bidwell's two sets of values are neither in agreement with each other nor with the results of Burgess and Waltenberg.[327] The latter determined the relative emissivity for 0.65μ of high-purity iron by means of the micropyrometer and obtained the following average values:

State	Temperature, °C.	Emissivity, per cent
Solid.............	1050	37.9
	1350	37.2
	1450	36.3
	1530	36.0
Liquid...........	1535	36.5
		Av. 36.8

The rounded value 37 per cent has been generally accepted as the best available for both solid and liquid high-purity iron.

Owing to the industrial importance of pyrometric control in many phases of the steel industry, a large number of determinations has been made of the emissivity of iron and steel of commercial purity, under conditions of plant operation. Such determinations usually were made on liquid steel which contained slag and various floating objects, or on solid iron or steel in the course of hot-working operations, while the surface of the metal was covered with a scale of iron oxide. Detailed discussion of these results does not belong in a monograph on the properties of high-purity iron; suffice it to say that emissivities between 40 and 45 per cent, for liquid metal or for solid metal with a

bright surface, and as high as 90 per cent, for solid metal with an oxidized surface, have been reported.

147. X-ray Absorption.—Data on the X-ray absorption of iron were summarized by Compton,[655] who also selected values based on averages of the available data. Additional values were reported by Martin[622] and have been added to Compton's data, in Table 63.

TABLE 63.—X-RAY ABSORPTION FOR IRON*

| Wave length, microns | Investigator | | | | | | | | Compton's selected values |
	Allen (540,546,547)	Hewlett (435)	Ahmad (539)	Ishino (376)	Richtmyer and Warburton (530)	Bragg and Pierce (299)	Martin (622)	Barkla (228)	
0.017			0.0575	0.0632					0.058
0.057									0.08
0.080	0.232								0.232
0.100	0.275								0.265
0.125	0.404	0.399			0.39				0.399
0.150	0.580	0.585			0.55				0.572
0.175	0.79	0.82			0.77				0.79
0.200	1.07	1.06			1.06				1.07
0.250	1.98	1.88			1.90				1.93
0.300	3.30	3.09			3.15				3.18
0.350	5.02	4.77							4.94
0.400	7.25	7.02							7.17
0.500		13.90				15.2			14.3
0.600		22.6				24.3			23.3
0.700	36.7	35.3					36†		36.3
0.800		50.7					53†		51.7
0.900	70	68.2				68.0	74†		69.6
1.00	102	90.2				93	93†		95.0
1.10	131					125	130†	121	126
1.32	230					205	215†		220
1.40	270						250†	268	270
1.54							316†		
1.66							416†		
1.76	57							67	60
1.93							68.8†	66	67
2.25								104	104

* Compton.[655]

† Not included in Compton's selected values.

D. AUTHORS' SUMMARY

The rounded value of 7.87 g. per cu. cm. appears to be the best present approximation for the density of iron at room

temperature. A greater number of significant figures can be given for the result of a single determination, but such precise determinations apply only to small, individual specimens. This rounded value for the density at room temperature is a summation of results obtained by direct determination, by extrapolation, and by computation from X-ray data for the lattice constant. The available data do not justify selection of probable values for the density of iron at elevated temperatures.

The compressibility of iron at 30°C. (85°F.) and at 75°C. (165°F.) for a range of pressure from 0 to 12,000 kg. per sq. cm., is shown by the data of Bridgman.[463]

The emissivity of both solid and liquid iron of high purity is about 37 per cent; available information in regard to the reflectivity and X-ray absorption of iron is summarized in Fig. 66 (p. 277) and Table 63 respectively.

CHAPTER IX

CHEMICAL PROPERTIES

Electrochemical Properties—Atmospheric and Gaseous Corrosion— Corrosion in Aqueous Solutions—Underground Corrosion—Effect of Impurities and Added Elements—Authors' Summary

From the metallurgist's point of view the most important chemical reactions which involve iron are those which are concerned with the permanence or lack of permanence of the metal. The reactions vary with the conditions of exposure but any attack on or deterioration of the iron may be broadly classed as corrosion. Consideration in this chapter is limited to the corrosion of iron in the atmosphere, in gases, in aqueous solutions and underground, and to the effect of impurities and added elements upon such corrosion. Before proceeding to this discussion, it is first necessary to view briefly the important facts on the electrode potential of iron and on overvoltage and passivity.

A. ELECTROCHEMICAL PROPERTIES

The electrode potential of a metal is a measure of the tendency of that metal to go into solution with the formation of ions, *i.e.*, to participate in chemical reactions. The tendency varies from a relatively high value for the alkali and alkaline earth metals to exceedingly small values for the noble metals such as gold and platinum. The escape of positively charged ions from the metal to the solution sets up a potential difference, between the negatively charged metal and the positively charged solution, which is proportional to the number of ions evolved. These potential differences, or rather the reverse potential differences which must be applied to prevent the solution of the metal, can be measured with reference to a standard such as the hydrogen or calomel electrode. The results of such determinations make it possible to arrange the metals in order of their decreasing

tendencies to go into solution, approximately as follows: potassium, sodium, barium, strontium, calcium, magnesium, aluminum, manganese, zinc, chromium, iron, cadmium, cobalt, nickel, lead, tin, hydrogen, bismuth, copper, antimony, arsenic, mercury, silver, palladium, platinum, gold, silicon, tantalum, tellurium, boron, tungsten, molybdenum, vanadium.

148. The Position of Iron in the Electrochemical Series.— In such a series any metal should displace from solution any other metal lower in the series, or if a pair of metals is connected together and immersed in an electrolyte, the less noble metal should dissolve preferentially and thereby protect the more noble metal from attack. This is generally true, for example zinc protects iron from corrosion. Lead, however, can protect iron only through its action as an unbroken envelope (if the envelope is broken to expose iron to the electrolyte, intensified corrosion of the iron will result due to the cathodic action of lead to iron). However, the position in the series of several of the metals may be radically altered by factors such as passivity, hydrogen overvoltage, or ionic concentration. For example, passive iron behaves as a more noble metal than is indicated by its position in the series. The electrode potential of a metal depends upon the concentration of metal ions in solution, hence the change from a strong to a weak electrolyte in general lowers algebraically the electrode potentials of all metals, due to the decreased ionization of the solutions. The decrease in potential is inversely proportional to the valence for equal changes in metal-ion concentration and depends upon the specific ionization of metal salts; therefore, it is not necessarily the same for all metals.

Instances of variations or reversals of the usual electrochemical relations of pairs of metals have long been known. Friend[235] stated that Avogadro in 1823 drew attention to the fact that when bismuth and iron are connected to a galvanometer and then plunged into concentrated nitric acid there is a deflection first in one direction and then in the other. In dilute nitric acid the same original deflection occurs and persists, without subsequent reversal. These results apparently are due to passivity phenomena at the surface of one or both of the electrodes. Variations in solution tension at different points on the surface of a piece of iron, due to stresses at the surface or to irregularities in

composition, can often be demonstrated by means of the ferroxyl reagent.[209]

According to the usual order of the electrochemical series, cadmium, lead, and tin are all cathodic to iron, yet Evans[778] found that cadmium was always anodic to iron in distilled water, tap water, M/10 sodium sulphate and M/10 sodium chloride solutions; lead was slightly anodic to iron in distilled water, and was variable in the other media depending on factors such as time and aeration; even tin was slightly anodic to iron when freshly immersed in distilled or tap water. The difference between the practical behavior of metallic couples and the behavior which might be anticipated from their positions in the ordinary electrochemical series was discussed by Rawdon,[802] who found that chromium did not furnish electrochemical protection for iron, but, probably on account of passivity, behaved as a neutral coating which neither inhibited nor accelerated corrosion. Aluminum behaved much like chromium. Cadmium plugs inserted in blocks of electrolytic iron and steel were deeply etched in sodium chloride solution indicating that under the conditions of these experiments cadmium was definitely anodic to iron, notwithstanding their positions in the electrochemical series. The relative positions of cadmium and iron have long been a subject of controversy as has the relation of iron and tin.[729,790,791,795] Predictions regarding behavior under corroding conditions should be based on an electrochemical series determined for those specific conditions.

The single potential of a metal cannot be measured directly but must be determined with reference to another electrode. Although the absolute value of the solution pressure of iron cannot be calculated or determined,[545,700] the value with reference to the hydrogen electrode can be measured. The fact that the solution pressure is definitely greater than that of hydrogen, irrespective of the absolute values, is the important point from the aspect of corrosion of ferrous materials.

149. Electrode Potential of Iron.—As might be expected, early determinations of the solution potential of iron, with respect to a standard electrode, yielded variable results depending upon the composition of the iron and upon experimental conditions such as the ionic concentration. To avoid the latter difficulty it is customary to express results in terms of a normal concentra-

tion of ions, computing this value from observations made with dilute solutions. The variation of potential with the concentration of the solution is illustrated for both hydrogen and iron by experimental results reported by Evans[554] as follows:

Normality	N	N/10	N/100	N/1000	N/10,000
Iron, Fe^{++}............	−0.34	−0.37	−0.40	−0.43	−0.46 volt
Hydrogen, H^+...........	0.000	−0.058	−0.116	−0.174	−0.232 volt

Evidently iron is anodic to hydrogen over a wide range of concentrations.

The International Critical Tables[834] adopted the value −0.44 volt (referring to the normal hydrogen electrode) for the equilibrium electrode potential of iron at 25°C. in contact with a solution containing a normal concentration of ferrous ions. This value, accredited to the work of Lewis and Randall, was substantiated by Hampton.[665]

The effect of tensional and torsional stresses on the potential of Swedish charcoal iron was reported[169] to be very slight although in some instances the potential of the strained metal was slightly lower (more anodic) than that of the unstrained material. The potential of highly purified iron in a solution of ferrous sulphate was found to be altered only slightly by application of a magnetic field but a trace of ferric ions had a pronounced effect.[577] A study[896] of the effect of hydrogen-ion concentration on the electrode potential of iron (0.18 per cent total reported impurities) led to the conclusion that, in solutions of potassium chloride or potassium phosphate, the change of potential with pH was not continuous. Another investigation[875] indicated that, in the presence of various anions, variation in pH from 1.00 to 6.95 resulted in irregular variation of the potential of a soft iron anode. The tendency of some of these anions to induce passivity phenomena perhaps influenced the results, as a recent investigator[985] concluded that the potential of electrolytic iron, in a 1 per cent solution of sodium sulphate, is a function of the pH, becoming more negative (more cathodic) when the pH is increased. Bodforss,[960] using carbonyl iron, also concluded that the potential of iron in aqueous solutions and at ordinary temperatures was a straight-line function of the

hydrogen-ion concentration, and Liebrich[975] found a similar relation in solutions of hydrochloric acid. Travers and Aubert[985] also cited experiments to show the effect of occluded hydrogen on the potential of electrolytic iron. Lochte and Paul[1015] reported that the potential of iron varies with the size of the electrode, the concentration of oxygen, the amount of stirring, and with the presence of anions such as Cl′ and $PO_4′′′$.

Working with both single-crystal and polycrystalline iron, Iwase and Miyazaki[785] observed interesting time-potential relations. The single-crystal specimen and a coarse-grained polycrystalline specimen were of the same stock which contained the following percentages of impurities: 0.40 per cent manganese, 0.021 per cent sulphur, 0.021 per cent phosphorus, and a trace of silicon; it contained no carbon. The specimens were immersed in N/10 solutions of ferrous ammonium sulphate and were connected to a N/10 calomel electrode which served as the zero of reference. The results showed that the potential of the single crystal rose rapidly to a maximum value (-0.728 volt) and thereafter remained constant. On the other hand, the potential of a polycrystalline electrode of the same iron rose rapidly to about the same maximum value (-0.726 volt) but after reaching the maximum fell off rapidly with increasing time. Iwase and Miyazaki regarded the final value obtained from the single crystal as the true potential for this iron and solution, measured against a calomel electrode. The initial rise in the curves was ascribed to solution of the electrodes in reaching equilibrium with the electrolyte; the subsequent fall in the curve for polycrystalline metal was ascribed to contamination of the surface of the specimen. However, Endo and Kanazawa[924] in similar experiments found that the potential of polycrystalline iron rose to a maximum value and subsequently remained constant, as did single-crystal iron. Their results against a normal calomel electrode were as follows:

Potential of a single crystal of iron............ -0.689 volt
Potential of electrolytic iron................. -0.691 volt
Potential of Armco iron..................... -0.693 volt

Aitchison[343] found that the solution pressure of iron crystals (in steel) varied with their orientation. In discussion of Aitchison's paper, Stead confirmed Aitchison's conclusions with the statement that for any aggregation of iron crystals in dilute

nitric acid, copper ammonium chloride, etc., the crystals with cube faces parallel to the surface had the lowest solution potential, *i.e.*, were cathodic to other orientations.

150. Summary of Data for the Electrode Potential of Iron.— The solution pressure of iron is greater than that of hydrogen, *i.e.*, iron tends to dissolve in and to displace hydrogen from aqueous solutions. A measure of this tendency can be expressed only with reference to a standard electrode such as the hydrogen electrode. Recent work indicates that the single potential of iron, in contact with a solution which is normal in respect to the concentration of ferrous ions, is -0.44 volt, referred to the normal hydrogen electrode.

The magnitude of the solution potential is affected by the concentration of hydrogen, ferrous, and ferric ions, and by the presence of certain anions, but is not affected to an appreciable extent by tensional or torsional stresses or by the presence of a magnetic field. The solution potential of iron varies with the orientation of the crystal; the cube faces have the least tendency to dissolve and consequently are cathodic to other orientations.

151. Overvoltage.—The composition and physical condition of either anode or cathode, or both, frequently affect the potential necessary to maintain an electrochemical reaction. For example, hydrogen can be deposited at a lower voltage on an electrode of platinized platinum than on other metals, including smooth platinum. Similar conditions are encountered at the anode in the deposition of anions such as oxygen.[858] Metallic ions in general are less subject to overvoltage phenomena than are the gaseous ions. The definition commonly employed[930] for overvoltage is as follows: Overvoltage of a gas upon a specified electrode is the polarization involved in the evolution of that gas on that electrode at a specified current density.

Overvoltage is due to the effect of the electrode on the reaction by which electrically charged ions give up their charges to the electrode and are converted into neutral atoms or molecules, or on the reverse reaction which converts neutral atoms or molecules into charged ions. In the case of hydrogen, overvoltage is due to polarization by electrically neutral monatomic hydrogen.[700] Hydrogen is evolved as gas or dissolved by the solution only as the infinitely small amounts of monatomic hydrogen, presumably adsorbed on the surface, react to form molecular hydrogen.

The cathodic overvoltage of iron has been shown to be a small but appreciable factor since it required 0.64 to 0.65 volt to deposit iron at ordinary temperatures on platinum or mercury cathodes.[101] This deposition potential is approximately 0.2 volt greater than the electrolytic solution potential, *i.e.*, the overvoltage of iron at platinum or mercury electrodes is approximately 0.2 volt.

There are practically no data available in regard to the effect of temperature on the overvoltage of iron. Ghosh[369] concluded that the phenomenon of overvoltage in an aqueous solution disappeared at 96°C.

The overvoltage of hydrogen increases with increasing current density[518,885] but is not affected by changes in pressure.[834] Data regarding the effect of these factors on the overvoltage of iron have not been encountered. The approximate overvoltage of hydrogen at the surface of iron and other metallic cathodes at low current densities is shown in Table 64. These data were obtained by Evans;[659] the results of other investigators, for example Knobel,[518] usually place the metals in the same order, but the numerical values vary with the experimental conditions.

TABLE 64.—APPROXIMATE OVERVOLTAGE OF HYDROGEN ON DIFFERENT CATHODE MATERIALS*

Cathode Material	Approximate Overvoltage, Volts
Platinum (blackened)	Very small
Platinum (bright)	0.1
Gold	0.02
Iron	About 0.05 in alkali; in acid solution it seems to be distinctly higher, probably about 0.2 volt
Silver	0.1
Nickel	0.15
Copper	0.25
Cadmium	0.5
Tin	0.5
Lead (smooth surface)	0.6 (smaller for spongy lead)
Zinc	0.7
Mercury	0.8

* Evans.[659]

152. Summary of Overvoltage of Iron.—The overvoltage of metals in general is small. For iron it is perhaps 0.2 volt at room temperature and decreases with increasing temperature to a

minimum at about 95°C. (205°F.).   However, overvoltage is one of the factors to be considered in the selection of operating temperatures for the production of electrolytic iron.

The overvoltage of hydrogen at the surface of iron is only a fraction of a volt in acid solution and is even lower in alkaline solutions.   However, even these small values may have a decided influence on the course of corrosion.

153. Passivity of Iron.—The passive state, produced in a metal by previous exposure or treatment, causes it to behave as a more noble metal; it is more resistant to solution and to corroding media than would be expected from its normal position in the electrochemical series.

The phenomenon of passivity in iron has long been recognized. One of the first observations was ascribed[362] to Kier, who in 1790 noted the passivity of iron in concentrated nitric acid. Many other solutions, in addition to nitric acid, may develop passivity in iron immersed in them, for example, solutions of silver nitrate, lead nitrate, mercuric nitrate, potassium permanganate, potassium dichromate, chloric acid, chromic acid, arsenic acid, sulphuric acid containing nitrous oxide, copper potassium tartrate, and ammoniacal copper solutions.   Iron is frequently rendered passive by anodic treatment.   It may be induced by exposure to compressed nitric oxide or to the vapors of strong nitric acid, and a certain degree of passivity, at least for the purer forms of iron, results from exposure to the oxygen of the atmosphere.

The two tests most commonly applied to identify the passive state in iron are immersion in a solution of a copper salt (usually copper sulphate) or in approximately 6 N nitric acid.   Active iron precipitates copper from a solution of a copper salt; passive iron does not.   Active iron dissolves in approximately 6 N nitric acid; passive iron does not.   Observation of immunity from rusting and the determination of anode potential have been employed to distinguish between active and passive iron.

As might be expected from the number of the media which can develop passivity in iron, there are varying degrees of passivity and of stability of the passive state.   Furthermore, the change from the active to the passive state usually is gradual.   If iron is immersed in strong nitric acid, there is usually a momentary action before the metal becomes passive.   Avogadro was

reported[235] to have observed, in 1823, the momentary activity, followed by passivity, of iron coupled with bismuth and immersed in concentrated nitric acid. Likewise, the reverse change from the passive to the active state may occur slowly; a piece of iron may remain inert for a considerable length of time in a solution of a copper salt but eventually become active and precipitate copper from the solution. Bennett and Burnham[362] stated that in general the time necessary to develop the passive state varies inversely with the oxidizing power of the medium; for example, if the metal is made the anode, the time required for passivity varies inversely with current density except that at low densities (anode voltage less than 0.65 volt) iron in sulphuric acid does not become passive at all. Evans[823] also stated that the passage from the active to the passive state (of iron) is a gradual one, the time varying from a few minutes to several hours depending on the degree of abrasion of the surface.

Metal which is passive toward copper nitrate is not necessarily passive to copper chloride or even to copper sulphate solutions. Iron, subjected to anodic treatment at low current densities, will dissolve, but high current densities lead in general to passivity. Intermediate densities sometimes permit a rhythmic fluctuation between the active and passive conditions. The current density needed to produce passivity on an iron anode varies with the nature of the solution. In nitrate solutions where the anions have a distinctly oxidizing character, a low density suffices; in chloride solutions it is difficult to produce passivity at all. In alkaline solutions passivity appears readily; in acid solutions a high current density must be applied before passivity sets in.[823] Spontaneous alternation between the active and passive state can also be obtained[362] when iron is immersed in nitric acid of about 1.3 specific gravity. During such periodic action, the time intervals usually are longer for the passive state than for the active state. Hedges[666] found that periodic passivity of iron could be obtained in sulphuric, nitric, or phosphoric acid solutions by adjusting the concentration and current density. Karschulin[1058] observed that electrolytic iron developed periodic passivity in solutions of mixed chromic and sulphuric acids and found that the frequency and amplitude of the fluctuations varied with the concentration of both acids and with additions of potassium sulphate.

Evidently the passive state is not particularly definite or stable except in the presence of the medium which induces it.   Bennett and Burnham[362] described various ways in which the passive state might be destroyed, Evans[824] described the breakdown of immersed films, and Speller[686] summarized the matter as follows:

In general when a passive metal is removed from the passivifying agent, it may continue in this state under favorable conditions for a considerable length of time, but the effect is not permanent.   The metal so passivified reverts to its normal condition if it is abraded, hammered, heated, exposed to a magnetic field under certain conditions, immersed in solutions of the halogen acids or salts, or brought in contact with an active metal, particularly if it is cathodic to this metal.

154. Theories of Passivity.—Several theories were formulated and considerable controversy ensued with regard to the mechanism of the change from the active to the passive state.   These theories were reviewed by Bennett and Burnham and more recently by Chittum.[875]   The oxide-film theory appears to have been most generally accepted; it postulates that passivity is due to the formation of an oxide envelope which is insoluble and usually invisible.   Objections to the oxide-film theory were based on the assumption that none of the common oxides of iron possesses the properties of passive iron.   To sustain it, the hypothesis was proposed[362,875] that passivity was due to some higher oxide, perhaps FeO_2 or even FeO_3.   Other objections were based on the apparently identical values for reflectivity and for X-ray examination of active and passive iron, on the invisibility of the oxide film, and on various phenomena such as the development of passivity in both acid and alkaline solutions.   The results obtained by Evans and his coworkers removed many of these objections to the oxide-film theory.   They have shown[711,826] that the passive film on iron, although normally invisible, nevertheless can be removed from the iron and thereby made visible, assuming that the film is not altered by the process of removal.

In another paper[823] Evans discussed the composition of the passive film, as follows:

It has been objected that the passivity of iron towards nitric acid cannot be due to an oxide film, since any oxide, it is alleged, would be dissolved by the acid.   This objection has been entirely disposed of by a delightful piece of research carried out at Bedford College, London,

by Hedges, who showed that—in point of fact—ferric oxide (if freshly ignited and therefore free from hydroxide) is not dissolved by concentrated nitric acid at ordinary temperatures; on raising the temperature, the dissolution first becomes appreciable at just the temperature at which metallic iron begins to be attacked by nitric acid of the concentration in question. This points to the fact that the invisible film which normally protects iron from nitric acid is ferric oxide.

Evans believed that the oxide-film theory is in accord with the facts of passivity in acid and alkaline solutions.

Passivity may be induced by more than one kind of film; for example, it appears readily during electrolysis of alkaline solutions when the discharge of hydroxyl ions would tend to convert the surface layer of the metal to insoluble oxide or hydroxide. Travers and Aubert[984] found that oxygen (dissolved) was essential to the development of passivity in alkaline solutions. The question of the optical properties of active and passive iron was studied by Freundlich, Patscheke, and Zocher[712] who found that there is a definite difference in the reflectivity of active and passive iron, passivity of their specimens apparently being due to a film about 10 Å. in thickness. In a recent study of the optical properties of iron mirrors, Tronstad and Borgmann[1073] concluded that the passive film on iron is about 25 Å. in thickness if it is formed by the action of nitric acid and somewhat less thick if formed by atmospheric oxidation. From these results it appears that, in previous work on reflectivity of active and passive iron, probably none of the samples was really active but all were more or less passivated by the action of oxygen of the air. Extraordinary precautions were necessary to obtain mirrors of active iron, in the work of Freundlich and his associates.

In spite of the excellent case made by Evans and other proponents of the oxide-film theory, some investigators believed that certain phenomena of passivity could be better explained by means of other theories. Müller[798] was not in entire accord with Evans' theories, particularly concerning the mechanics of the protective action of the oxide film. In another paper,[978] Müller's theories were applied to data obtained through the use of an oscillograph, to calculate separately the resistance of the pores and of the oxide film on an iron electrode passivated in neutral sodium sulphate solution. As the film became

thicker, the pores became smaller and their resistance increased; the resistance of the film also increased. An excellent review and bibliography of passivity are found in the recent edition of Abegg's Handbook.[914]

A practical application of passivity was described by Burgess,[114] who encountered difficulty in electrolytic stripping of a brass coating without attacking the underlying mild steel. The difficulty was solved by shifting to a sodium nitrate solution, in which the brass was completely removed by electrolysis, but in which the mild steel became passive and was not attacked. Some single-potential measurements were made, indicating that the potential of iron varied with current density up to a limiting point at which the metal became passive as evidenced by a sudden large increase in potential and the first evolution of oxygen at the anode. The results indicated that passive iron may be cathodic to platinum and approximately equal in potential to the peroxide plate of a lead storage battery.

It might be expected that the passive state would be more easily attained and more stable with increasing purity of the iron. This would follow primarily from the absence of non-uniformities in the structure which might form small local couples with the iron to destroy the passive film. Evans[823] found that iron of high purity became passive as a result of exposure to the atmosphere:

Short exposure to the air at slightly elevated temperature renders electrolytic iron unaffected by copper nitrate, but a similar short exposure to air at ordinary temperatures still permits the iron to deposit copper. . . . In the case of pure electrolytic iron it is actually found that after long exposure to dry air the power to precipitate copper from copper nitrate solutions is lost.

In similar experiments, steel samples did not exhibit air-induced passivity, but readily precipitated copper from solution. In another publication[659] Evans stated that electrolytic iron, immersed in water, which was saturated with oxygen, could be passivated by uniform aeration, whereas mild steel under similar conditions remained active and rusted. Schikorr[1027] also found that iron and its alloys become passive more readily as the homogeneity increases. Freundlich, Patscheke, and Zocher[712] worked with mirrors deposited from iron carbonyl and found it

difficult to protect high-purity iron, in this form, from the passivating action of the atmosphere. However, even with high-purity iron the passive state is not entirely stable, as Evans[823] recorded that no reaction occurred if a piece of "pure" iron was dipped in concentrated nitric acid, but if it was then removed and allowed to drain, violent reaction often commenced after a few seconds at the margin of the wetted area and spread over the whole surface.

155. Summary of the Passivity of Iron.—The practical importance of passivity of iron is summarized in the remarks of Speller: "If the metal could be maintained in this [passive] state, it would be of great practical value, but unless the metal can be kept in contact with a passivifying reagent, the effect is soon destroyed and the metal reverts to its former state." These remarks referred to irons of commercial purity but probably are equally applicable to high-purity iron. The latter is more easily rendered passive, and the passive state is perhaps more stable than for irons of lower purity. Nevertheless the passivity even of very pure iron probably cannot be depended upon for permanent protection against corrosion, except perhaps by very mild corroding agents.

B. ATMOSPHERIC AND GASEOUS CORROSION

The rusting of ferrous materials exposed to the atmosphere in the absence of protective coatings is almost universal. The economic importance of this form of corrosion is due to the fact that the deterioration, once started, usually is progressive and continuous. Estimates of the annual wastage in money and resources, due to the rusting of ferrous products, vary widely, but the fact that this annual loss is enormous is a natural corollary of the recent estimate of Tiemann[1032] that 80 per cent of all the steel in use is subject to atmospheric corrosion.

The deterioration of iron in the atmosphere is a complicated process, subject to the influence of a large number of variables. The presence of liquid water and of oxygen are of fundamental importance. The general effect of oxygen is to stimulate corrosion of iron, although occasionally oxygen may act as a deterrent by inducing passivity. Other factors which influence the rate and extent of atmospheric corrosion include sunlight, humidity, amount and frequency of rainfall, temperature, the

presence of solid matter, gases, acids, or salts in the atmosphere, the homogeneity and composition of the metal, passivity, the nature and amount of rust formation, and many others. Any one, or combinations of these, may, under certain conditions, become the dominant factor in determining the rate and extent of corrosion.

As a result of the complicated nature of corrosion, the number of variables concerned, and the variety of media in which corrosion can occur, a long time was required to develop a satisfactory theoretical explanation of corrosion in general. The direct-chemical-attack theory, acid theory, hydrogen-peroxide theory, colloid theory, electrochemical theory, biological theories, film theories, have been advocated with considerable vigor at one time or another. The electrochemical theory has survived better than the others[453] and is now regarded quite generally as supplying the most acceptable explanation for the greatest number of cases of corrosion. The exposition of the electrochemical theory published in 1924 by Bancroft[545] and the work of Evans[659] in developing the importance of oxygen-concentration cells are recommended to the reader. In the present text the corrosion of iron will be considered an electrochemical process under all conditions except for corrosion by oxygen and other gases at elevated temperatures, which is probably the result of direct chemical action.

156. Rate of Corrosion of Massive Iron in Dry Air.—According to the electrochemical theory of corrosion, an electrolyte* must be present, and according to the experimental results of many investigators liquid water must be present, in order that corrosion of iron may occur. There is universal agreement that in the absence of water and at temperatures below 150°C. (300°F.) the reaction between massive iron and air, or oxygen, is of negligible importance. Abegg[914] credits this observation to Berzelius in 1835. Friend[235] in 1911 stated that

. . . for many years it has been a matter of common knowledge that a piece of polished and bright iron may be kept for an indefinite time exposed to dry air without suffering the slightest diminution in metallic splendor, provided, of course, the temperature is not raised abnormally. . . . Even at 100°C. the action of air upon iron is indefinitely slow.

* A recent definition[980] is that an electrolyte is a conducting medium in which the flow of electric current is accompanied by the movement of matter.

Pollitt[576] stated as a fundamental fact: "Iron will not corrode or rust in dry air, *i.e.*, in the absence of moisture." The conclusion of previous investigators that dry air, or dry carbon dioxide, or mixtures of the two, at ordinary temperatures, did not cause corrosion of iron was confirmed by Hicks.[833] Evans[659] quoted calculations by Tammann which showed that exposure to dry air at ordinary temperatures might produce a visible oxide film on iron in 25×10^{17} years. Evans' own opinion was expressed as follows: "The time required to produce the first (yellow) interference tint at ordinary temperatures is too long to be determined by direct experimentation and probably exceeds the life of man." Evans' summary expresses the general opinion, as follows:

All ordinary metals, if perfectly dry, can be kept in pure, dry air indefinitely without undergoing visible change. It is probable that a film of oxide is quickly produced on the surface, and when it is still too thin to give even the first interference tint, it becomes practically impervious to oxygen, and thus ceases to thicken.

Vernon[748] concluded that, for indoor tests, the rate of rusting of iron was governed entirely by the presence of suspended dust particles in the air, and that rust was inhibited by filtering the air or even by screening the metal with a single thickness of muslin. In view of the evidence of other investigators, it appears probable that Vernon's dust particles were moist and that the ensuing corrosion was due to the moisture carried rather than to the dust particles themselves. In a recent paper, Vernon[1035] reiterated the important rôle of dust particles in promoting corrosion through the creation of local couples and surface discontinuities and called attention to the influence of particles of hygroscopic material, particularly ammonium sulphate, in stimulating corrosion even at humidities below the dew point.

157. Rate of Corrosion of Pyrophoric Iron.—Finely divided or porous iron produced by reduction of iron oxide with hydrogen is an exception to the general rule that iron is not attacked to an appreciable extent by air at ordinary temperatures. If iron oxide is reduced by hydrogen at relatively low temperatures, the resulting iron sponge is pyrophoric; on contact with air the iron is oxidized rapidly and completely, usually with an appreciable increase in temperature. Moisture present in the air may be

partly responsible for the initial stages of this oxidation, as suggested by Friend,[235] but it seems probable that the pyrophoric properties of sponge iron are merely an extreme case of surface phenomena. The surface area is enormous and is in a highly reactive state as indicated by the catalytic activity of sponge iron in such processes as the synthesis of ammonia. It is admitted that all iron is covered with a superficial layer of oxide acquired on first coming in contact with the air. In the case of ordinary iron, the heat generated by this superficial oxidation is negligible in comparison with the heat capacity of the massive iron. On the other hand, in sponge iron a large proportion of the total mass is affected by the superficial oxidation of the surface. Furthermore, heat is generated by this surface oxidation faster than it can be dissipated, which results in an increase in temperature of the mass with a consequent speeding up of the process of oxidation. The fact that the pyrophoric properties of sponge iron can be largely or completely destroyed by sintering the freshly reduced sponge is further evidence that the pyrophoric behavior is simply a case of surface phenomena, equivalent to the greater chemical activity of finely divided metals as compared with massive metals. The other extreme of surface phenomena is represented by the fact that polished surfaces of metal are most resistant to tarnishing.

158. Oxidation of Iron at Elevated Temperatures.—The oxidation of pyrophoric iron at normal temperatures or of ordinary iron at temperatures above 200°C. (390°F.) is an exception to the general rule that rusting of iron is an electrochemical process. It is generally agreed[235,505,545] that oxidation of iron at higher temperatures is the result of direct chemical combination of iron and oxygen; in fact some investigators, for example Pollitt,[576] refuse to consider this reaction as a form of corrosion. To justify this distinction between corrosion and oxidation at high temperatures, Pollitt pointed out that the product of ordinary corrosion was rust, which accelerated subsequent attack, whereas the product of oxidation at high temperatures was magnetic oxide, which retarded subsequent oxidation.

The direct oxidation of iron is negligible below 150°C. (300°F.),[191,235] but at higher temperatures iron discolors with visible formation of oxide.[914] Evans[659] discussed the formation of "temper colors" on iron and the work which has demon-

strated that the colors of these oxide films are interference colors. He concluded that the rate of oxidation at high temperatures was determined mainly by the rate of diffusion of oxygen through the film and called attention to the fact that oxidation at high temperatures was a complicated matter, involving composition of scale, solid solution of oxygen in iron, and other variables. Oxygen might affect iron in two ways: form a solid solution in the iron or, penetrating along the grain boundaries, form oxide envelopes around the grains.

Detailed study of the oxidation of electrolytic iron (0.01 per cent carbon, 0.005 per cent manganese, 0.02 per cent silicon) and of Armco iron at temperatures between 700 and 1000°C. (1290 and 1830°F.) was made by Pilling and Bedworth.[529] They found that the oxide formed at these temperatures was normally slaty black and was formed in two phases, a thick outer and a thin inner layer, with an aggregate composition intermediate between Fe_3O_4 and FeO (equivalent to 60 per cent FeO and 40 per cent Fe_3O_4). Irregularities in the oxide coatings indicated local reactions other than those of oxidation in the simplest sense. Electrolytic iron was particularly susceptible to this irregular attack. Armco iron oxidized at a consistently faster rate and formed coatings which in general were smoother than those on electrolytic iron. The amount of oxidation at 800 to 1000°C. (1470 to 1830°F.) was nearly twice as great in oxygen as in air. Some of Pilling and Bedworth's data are as follows:

Material	Atmosphere	Temperature		Oxidation rate, g. per sq. cm. per hr.
		°C.	°F.	
Armco iron.	Air	800	1470	1.06×10^{-4}
		900	1650	$4.9 \ \times 10^{-4}$
		1000	1830	$20.5 \ \times 10^{-4}$
Armco iron.	Oxygen	800	1470	1.95×10^{-4}
		900	1650	$10.1 \ \times 10^{-4}$
		1000	1830	$43.0 \ \times 10^{-4}$
Electrolytic iron.	Oxygen	700	1290	0.17×10^{-4}
		800	1470	1.00×10^{-4}
		900	1650	$6.5 \ \times 10^{-4}$

These results, in general, were confirmed by the recent work of Portevin, Prétet, and Jolivet.[1068]   A study of the effect of time and temperature on the formation of scale on commercially pure iron and alloys was made by Heindlhofer and Larsen.[1003]

159. Corrosion by Moist Air.—Atmospheric corrosion of iron, in the ordinary sense of the term which implies the formation of visible rust, occurs only in the presence of water. Speller[686] stated that the amount of corrosion was controlled mainly by the amount of moisture and cited statements by Evans[506,659] and by Vernon[537] that corrosion could occur when only an adsorbed film of water was present.   Such a film was invisible and might be formed when the moisture in the air was below the saturation point.   Bancroft[545] reviewed the work of Friend, Dunstan, and other investigators who showed that rusting of iron did not occur in the presence of either moist oxygen, carbon dioxide, or mixtures of these gases, provided the temperature remained constant.   However, if the temperature was allowed to fluctuate so that a film of liquid water might condense on the metal, rusting occurred in the presence of oxygen alone or in mixtures of oxygen and carbon dioxide.   In further experiments high-purity iron and oxygen were left in contact with dry ether instead of water.   In this case no rusting occurred. "It is therefore concluded from the results of all these experiments that liquid water is essential for the rusting of iron and that the chemical action involved is the reduction of the water by the iron."   These conclusions were accepted by authors such as Pollitt,[576] Hicks,[833] and Abegg.[914]   Indications of the importance of the presence of water were furnished by Vernon,[537] who called attention to the fact that polished iron resisted ordinary atmospheric exposure but rapidly lost reflectivity in the presence of rain, and by Friend,[236] who pointed out that oil films may be quite permeable to oxygen and still afford protection to iron because they are impermeable to water.

160. Corrosion by Water Vapor.—Corrosion of iron by water vapor is somewhat analogous to the action of dry air at corresponding temperatures.   At ordinary temperatures water vapor does not cause corrosion of iron; liquid water must be present. At higher temperatures, however, steam and water do react with iron.   In some of his early papers, Friend reported[239] that iron and steam apparently began to react slowly at temperatures as

low as 150°C. (300°F.) and more rapidly as the temperature was raised. Powdered iron began to react to a noticeable extent with steam at temperatures as low as 240°C. (465°F.). Between 200 and 1200°C. (390 and 2190°F.) the reaction was believed to follow the reversible equation:

$$3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 2H_2$$
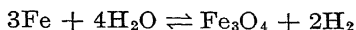
High-purity iron foil was not attacked at 250°C. (480°F.) by steam which was free from carbon dioxide[239] but was noticeably tarnished at 350°C. (660°F.)[191] and at 400°C. (750°F.).[235] However, even at 500°C. (930°F.) the reaction between high-purity iron and steam was only superficial and quite slow.

The difference between the attack of wet and dry steam has been emphasized recently. Pollitt[576] concluded that the action of steam at high temperatures was comparable to that of dry air at the same temperatures and resulted in the formation of a thin film of Fe_3O_4. He pointed out that the blades of a steam turbine do not corrode since they are protected by a film of Fe_3O_4. Corrosion begins where the steam becomes wet. Similarly the corrosion of steel superheater tubes is generally confined to the inlet or wet end and does not extend beyond the point where the steam becomes dry. However, iron valves are not recommended for superheated or high-pressure steam.[501] Speller[686] concluded that pure dry steam did not attack iron pipes up to 540°C. (1005°F.) or probably a little higher, and that among the variables to be considered were the amount of excess air in the steam, sulphur compounds in the gases, velocity and temperature of the gas, impingement of flames, abrasion from solids in the gas stream, and so on.

161. Effect of Purity of Iron on Atmospheric Corrosion.— The resistance of even the purest irons to atmospheric corrosion is apparently due more to factors such as passivity than to purity. Abegg[914] called attention to the extreme passivity of very pure irons and to the fact that application of mild pressure to such an iron may suffice to cause rusting. Burgess and Aston[274] found that an average grade of electrolytic iron, when exposed to the atmosphere, corroded more than commercial ferrous products and more than most of the alloys prepared from it. During 162 days' exposure to the atmosphere this electrolytic iron lost 0.10 lb. per sq. ft. of surface.[274] This material was

"not the purest electrolytic iron that could be produced," but Richardson[447] stated that even the purest obtainable electrolytic iron has been found to be "highly corrodible" in the presence of oxygen or air. The actively stimulating action of small amounts of certain impurities, on atmospheric corrosion, was mentioned in discussing the preparation of electrolytic iron in chloride and in sulphate baths. Iron from chloride baths is much more subject to rusting than iron of comparable purity prepared in sulphate baths, the difference being ascribed to the presence of residual traces of chlorides. Hughes[516] also discussed the corrosion of iron from chloride and sulphate baths.

On the whole, it appears that purity is not the determining factor in resistance to atmospheric corrosion. All forms of iron are attacked, and any difference due to composition is merely a difference in rate of attack. Pilling and Bedworth[529] found that electrolytic iron in air at 700 to 1000°C. (1290 to 1830°F.) was oxidized at a consistently slower rate than Armco iron, and Kenyon[787] found that Armco iron withstood furnace gases at 760 to 900°C. (1400 to 1650°F.) better than mild steel, due to the fact that the scale on Armco iron was tightly adherent, whereas the scale on mild steel was loose and easily flaked off. Friend[828] found that wrought iron and mild steel were attacked to about the same extent during 7 years' exposure to the atmosphere; Stoughton[491] reported that wrought-iron pipe exposed to the atmosphere corroded 2.6 times as fast as electrolytic iron, and Speller[686] cited the tests of the American Society for Testing Materials which showed that open-hearth iron was not noticeably superior to wrought iron or steel. There is no definite relation between resistance to corrosion in the atmosphere and in other media. Aupperle and Strickland[425] stated that metals which resisted atmospheric corrosion for several years subsequently lost several times as much weight in the immersion test as did materials which failed first in the atmospheric test.

For many years it was customary to cite the Delhi pillar, and other specimens of ancient iron which had resisted corrosion over long periods of time, as illustrating the effect of purity and proving that the products of the ancient workers in metal were superior to those of modern times. However, about 1910 the point of view began to change. Cushman and Gardner[209] quoted Walker's conclusion that iron equal to that of our fore-

fathers could be made by modern methods. Hadfield[259] investigated the history and composition of various specimens of ancient iron, including the famous Delhi pillar. The latter contained 0.080 per cent carbon, 0.046 per cent silicon, 0.006 per cent sulphur, 0.114 per cent phosphorus, and no manganese, and had a Brinell number of 188. According to Hadfield, this material, which had withstood atmospheric exposure since about 300 A.D., was hardly a "pure" iron in the modern sense of the word, but was in fact an excellent type of wrought iron. Furthermore, the resistance of this material to atmospheric corrosion for so long a time probably was due more to the mildness of the corrosive attack than to the corrosion resistance of the metal. Pollitt[576] and Rosenhain[335] reported that various samples of ancient iron, which had previously withstood exposure to the atmosphere of India or Egypt for hundreds and even thousands of years, when brought to England and exposed to the atmosphere there, corroded as rapidly as modern products. Walker[454] cited the case of an old bridge, as follows:

The public is still told through advertising propaganda that the old Newburyport bridge withstood Atlantic Ocean storms for over one hundred years because the iron from which it was built was pure and homogeneous, when, as a matter of fact, the majority of the links of the great chains were very impure and extremely heterogeneous. The further fact that when these very pure links were rolled down to sheet form and exposed to the weather, they rusted like modern iron and disappeared in a few years, is conveniently ignored.

Speller[686] examined specimens of iron pipe which had survived 20 years of exposure to the atmosphere in Panama. Some of the pipes were in excellent condition, others, of the same chemical composition, were badly rusted. If the surface was removed from one of the apparently resistant pipes, the newly exposed surface promptly began to rust "just like modern steel." Speller believed that the resistance to corrosion of some of these pipes was accidental, perhaps due to initial exposure during a long, dry, hot period, in which a protective film, perhaps of dry oxide, developed. On the other hand, if initial exposure occurred during a wet season, the initial product of corrosion would be hydrous ferrous oxide, quite different from the anhydrous oxide in its effect on subsequent corrosion. Richardson[446] compared old irons with modern products during 2 years' exposure to the

atmosphere and found no difference. Friend and Thorney-croft[608] compared modern mild steel with pieces of excavated Roman iron, in alternate wet and dry tests. Both metals corroded. The same authors[556] compared old iron from India and Ceylon with modern mild steel in alternate wet and dry tests and in sea water. Again the old irons corroded just as did modern mild steel. Evidently the survival of these old irons was due to the conditions of exposure or to unusual surface effects rather than to the purity or inherent resistance of the metal itself.

The effect of small amounts of impurities or added elements on the resistance of iron to atmospheric corrosion usually appears to be only a minor variable. The result of small changes in composition usually is less important than minor variations in the conditions of corrosive attack. Real resistance of iron to atmospheric corrosion is achieved only through the addition of elements such as chromium, nickel, or silicon in amounts such that the resulting steels or cast irons are far removed from pure iron. An exceptional case where a small amount of an added element exerts a marked effect on the corrosion of iron is the addition of copper. The presence of 0.15 to 0.25 per cent materially increases the durability of iron in the atmosphere, not because the copper-bearing iron does not rust but because the initial rust film protects the underlying metal, whereas the initial rust film on non-copper-bearing iron permits and even stimulates subsequent corrosion. The effect of copper and of other impurities and added elements will be discussed in more detail in subsequent pages.

162. Corrosion by Gaseous Atmospheres.—Iron may be attacked, sometimes to a serious extent, by gaseous atmospheres which do not contain oxygen. Such an attack is not corrosion in the sense that it produces rust, but the deterioration of the metal may be fully as severe as that which is accompanied by rust formation.

Hydrogen penetrates iron readily. Under atmospheric pressure molecular hydrogen penetrates iron at elevated temperatures, and atomic hydrogen, generated by electrolysis or by chemical action, penetrates iron at room temperature.[807] Benton and White[958] reported that freshly reduced iron absorbs hydrogen at temperatures as low as $-183°C.$ ($-300°F.$). At

low temperatures the absorption was limited to the surface of the iron, but at 110°C. (230°F.) and higher solution was evident. Under pressure of 4000 atmospheres, according to Poulter and Uffelman,[979] hydrogen readily penetrated a very fine-grained steel at room temperature. At elevated temperature the penetration of solid iron by hydrogen results in the reduction of certain oxides, a fact which is utilized in the well-known Ledebur method for oxygen analysis. Decarburization also results from the penetration of steels by hydrogen.[973] Extended exposure of iron to the action of hydrogen, either dry or moist, at high temperatures eliminates carbon, reduces the amount of other impurities, and results in extraordinarily high magnetic permeabilities.[964] Messkin and Margolin[976] reported that hydrogen treatment of transformer steel may result in cracks, presumably formed by the escape of methane, steam, or other products of the reduction by hydrogen. Lewkonja and Baukloh[1014] found that the permeability of iron to hydrogen at 700 to 1000°C. (1290 to 1830°F.) increased with an increase in temperature or in carbon content and decreased with an increase in grain size or in wall thickness. Apparently hydrogen passes through the grain boundaries, and ferrite is less permeable than are other constituents of iron.

Iron is also subject to attack in atmospheres of nitrogen, and particularly in the presence of ammonia. Emmett and his coworkers concluded that iron prepared by reduction of the oxalate reacted only superficially with molecular nitrogen at temperatures between 400 and 700°C. (750 and 1290°F.), under pressures as high as 200 atmospheres,[879] but that in atmospheres of ammonia or of mixtures of ammonia and nitrogen the iron may be completely converted to Fe_4N.[919] Similar conclusions were reached by Gray and Thompson[968] who found that iron and molecular nitrogen react to some extent at temperatures as low as 500°C. (930°F.), possibly as low as 200°C. (390°F.), but that in the preparation of any quantity of iron nitride the use of an atmosphere of ammonia is desirable. In their experiments, powdered iron heated in nitrogen at 1000 to 1100°C. (1830 to 2010°F.) reached a constant weight after losing 0.3 to 0.4 per cent. The fact that the product of exposure to nitrogen at 500°C. (930°F.) or lower was a gray film, whereas at about 700°C. (1290°F.) the product was a fused transparent layer, was

suggested tentatively as being due to the fact that different products result from the action of nitrogen on alpha and on gamma iron. The thin film formed on electrolytic iron as a result of exposure to purified nitrogen at 700 to 1100°C. (1290 to 2010°F.) exerted an appreciable influence on the rate of solution in 0.5 N hydrochloric acid.[968]   Similar treatment of steel likewise produced a surface layer resistant to hydrochloric acid, and sometimes resulted in decarburization of the steel.[830] The ability of iron to absorb nitrogen at atmospheric pressure was reported by Sieverts[942] to range from 0.4 mg. of nitrogen per 100 g. of alpha iron at 750°C. (1380°F.) to 18.5 mg. per 100 g. of gamma iron at 1150°C. (2100°F.). Reaction of ingot iron and nitrogen at the temperature of the electric arc was studied by Willey,[811] who found that near the center of the arc 12 to 15 per cent of the iron was present in the form of iron nitride; at the outer edges of the arc the proportion fell to 6 or 8 per cent; and the sublimate obtained from the walls of the reaction chamber contained only 2 or 3 per cent of nitride. This indicated that iron nitride formed in appreciable amounts at arc temperatures but decomposed during slow cooling.

The fact that iron is an efficient catalyst for the synthesis of ammonia from mixtures of nitrogen and hydrogen, and for the reverse process of cracking ammonia into the constituent gases, undoubtedly is connected with the fact that iron reacts with both gases to a greater or less extent. Vanick[536] reported the destructive action of gaseous ammonia on iron at atmospheric pressure and elevated temperatures and found that the formation of stable iron nitride depended on the temperature. The action of the gases for the synthesis of ammonia on various ferrous materials was reported in a subsequent paper,[747] in which it was found that the presence of carbon enhanced the attack but that the presence of 2 per cent, or more, of chromium greatly reduced the attack. Recent papers on the catalytic action of iron in the synthesis or decomposition of ammonia are those of Winter,[952] Dixon and Steiner,[921] and Mittasch and Keunecke.[977]

Carbon dioxide at one time was considered to be the principal cause of corrosion of iron. However, Friend[235] reviewed the earlier work on which this assumption was based and concluded that condensed water might have been responsible for the action attributed to carbon dioxide. Friend found that the presence of

carbon dioxide stimulated corrosion by oxygen and water but concluded that carbon dioxide alone, either moist or dry, was not responsible. Abegg[914] agreed with this conclusion, but Pollitt[576] quoted Paul that in the presence of an excess of carbon dioxide and water, free or atmospheric oxygen was not essential to corrosion. In the discussion of aqueous corrosion, it will be shown that the corrosion of iron in water, in the absence of oxygen, is limited by the solubility of ferrous hydroxide. The action of carbon dioxide may be to convert some of the accumulated ferrous hydroxide to a more soluble compound. Corrosion of the iron could then proceed a little farther, but the action probably is less rapid than when oxygen is present.

In view of the particular efficacy of chloride ions in destroying passive films, it is interesting to note that dry gaseous chlorine is handled in iron or steel equipment, although if moisture or hydrochloric acid is present corrosion follows.

163. Summary of Atmospheric and Gaseous Corrosion.— In the absence of moisture, exposure of a fresh surface of iron to air or to oxygen results in the rapid development of a superficial coating of iron oxide. When exposure occurs at temperatures below about 150°C. (300°F.) the coating is so thin as to be invisible, yet it suffices to prevent further oxidation. An exception to the general rule is found in the case of certain irons which are pyrophoric, probably because their surface area is so great in proportion to the mass (see p. 295). At temperatures above 200°C. (390°F.) the rate and extent of the reaction between oxygen and iron increase with increasing temperature. The final product of this action is Fe_3O_4 which tends to protect the underlying metal. The attack at high temperatures is more severe in an atmosphere of oxygen than in air. Oxidation at high temperatures is the result of chemical combination, not electrochemical corrosion.

In the presence of liquid water iron exposed to the atmosphere corrodes with the formation of visible rust. Liquid water is essential to corrosion, but the amount need not be more than an adsorbed film. Iron does not rust in a slightly moist atmosphere which is maintained at constant temperature but rusts readily in the same atmosphere if the temperature is allowed to fluctuate so that condensation occurs. The presence of both oxygen and liquid water is essential for the occurrence of appreci-

able corrosion; other factors which influence the rate or extent of corrosion include temperature, humidity, the presence of rust, homogeneity of the metal, passivity, presence of foreign material in either the metal or the atmosphere, and so on.

Iron may suffer deterioration from exposure to other gaseous atmospheres. It is attacked by dry steam at elevated temperatures much as it is by dry air or oxygen, but rusting occurs only in wet steam. Iron may be appreciably attacked by atmospheres of hydrogen, nitrogen, or ammonia.

C. CORROSION IN AQUEOUS SOLUTIONS

The question of submerged corrosion of iron has received about as much attention as atmospheric corrosion, not because equal amounts of ferrous materials are involved (Tiemann[1032] estimated that only 10 per cent of the ferrous materials in use is subject to underwater corrosion), but because submerged materials are not readily subject to inspection. Consequently, if submerged corrosion once starts, it may readily proceed to completion before being observed.

In the discussion of atmospheric corrosion it was shown that iron is subject to corrosion in the presence of a combination of water and oxygen of the air. In considering corrosion in liquid media, where the supply of oxygen is much less abundant, the question arises whether or not iron is attacked by pure water in the absence of oxygen.

164. Corrosion of Iron in Water.—The electrolytic solution potential of iron is greater than that of hydrogen.[633] Consequently iron, when placed in a solution which contains hydrogen ions, displaces hydrogen and dissolves. In other words "iron should corrode in pure water, as indeed it does."[545] The rate at which it corrodes is low, since an iron ion can enter the solution only by displacement of a hydrogen ion, a very limited number of which is present in pure water (about 1 g. of hydrogen ions in 10 million liters of water, according to Cushman and Gardner[209]).

The amount of iron which can dissolve in pure water in the absence of oxygen is limited by the solubility of ferrous hydroxide, and is equivalent to 0.00117 g. of metallic iron per liter according to an early determination[467] and 0.00374 g. per liter according to a later investigation.[644] The solubility of iron ions varies with the hydrogen-ion concentration; Halvorson and Starkey[717]

reported that the amount of ferrous ions in solution varied from 27×10^1 parts per million of solvent at a pH of 3.0 to 27×10^{-7} parts at a pH of 7.0. The solubility of ferric ions under similar conditions is even less, decreasing from 6.1×10^1 parts per million at a pH of 3.0 to 6.1×10^{-11} at a pH of 7.0. Unless the hydrogen-ion concentration is artificially maintained, the dissolving of iron by displacement of hydrogen and formation of ferrous hydroxide tends to make the solution slightly alkaline. In a recent review, Hicks[833] concluded that iron will continue to dissolve in pure water, free from carbon dioxide and oxygen, until the pH value reaches 9.4, then solution ceases. He called attention to the importance, from a corrosion standpoint, of the solubility of iron in water: "A film of liquid water in contact with a metallic surface is prerequisite to the corrosion of that surface; water vapor is much less active, perhaps inactive, in the process, apparently pointing to the solvent action of water as the real cause of corrosion."

This almost negligible solubility of iron (3 or 4 mg. per liter of water) and the absence of visible rust doubtless led some workers to conclude that iron was not attacked by pure water alone. For example, Friend[467] reported a piece of Swedish iron which showed "very little change" after exposure for 20 years to pure water in the absence of air. However, Cushman[209] confirmed experiments of Whitney and Collins, showing that if the iron specimen was removed from the clear colorless water and air was subsequently admitted, rust quickly appeared in the water as a result of oxidation of the soluble ferrous hydroxide to the less soluble ferric compounds. Bancroft[545] suggested that the failure of some investigators to find any trace of iron in solution in pure water may have been due either to overvoltage or to passivity.

Surface characteristics and the degree of subdivision affect the rate of solution of a metal. Highly polished mirror surfaces are more resistant to corrosion than ordinary massive metal, and the latter is more resistant than the same metal in finely divided form. Several factors including passivity probably are involved in this relation of particle size and corrodibility. The corrosion rate even of high-purity iron is affected by particle size; Abegg[914] cited four investigators who found that hydrogen was generated by the action of water on finely divided iron and

five investigators who concluded that oxygen-free water did not react with compacted iron. Certain phenomena, which apparently must be related to surface characteristics, are difficult to explain. For example, McAulay and Bastow[846] reported that two apparently identical pieces of electrolytic iron, cut from the same sheet and having similarly ground surfaces, gave widely different potentials on immersion and had distinctly different subsequent histories.

. Enough positive evidence has been accumulated to justify the general conclusion that iron will dissolve to some extent in any water, even the purest water. In the absence of oxygen, the limit of solubility of iron in pure water is determined by the solubility of ferrous hydroxide, a small but definite amount.

165. Corrosion of Submerged Iron in the Presence of Oxygen. Although iron is not appreciably affected by exposure to water in the absence of oxygen, or to air at ordinary temperatures in the absence of water, the combined action of water and oxygen is primarily responsible for submerged corrosion, just as it is for atmospheric corrosion. This thought has been expressed by practically every writer on corrosion; for example, Speller[686] stated that "the presence of oxygen 'is essential for appreciable corrosion in ordinary water . . . oxygen and water will cause corrosion even in the absence of CO_2 or other acids . . . in natural waters corrosion is almost directly proportional to the oxygen concentration if other factors do not change," and Whitman[642] said that "the presence of dissolved oxygen is of primary importance for appreciable corrosion in so many cases. . . . " Richardson[421] reported that relatively pure iron corrodes at an extremely slow rate in the absence of oxygen but at a comparatively rapid rate in the presence of oxygen. Tiemann[1032] believed that in underwater corrosion the controlling factors are oxygen concentration, hydrogen-ion concentration, composition of the water, rate of motion, temperature, and protective scale formation.

Serious corrosion of iron therefore requires the presence of both liquid water and oxygen. The water furnishes the electrolyte in which iron dissolves with the displacement of hydrogen and through which current flows from the areas which are being attacked to the cathodic areas. Oxygen dissolved in the electrolyte serves in several ways to stimulate and intensify corrosion

attack. One of the most important functions of oxygen is to serve as a depolarizer, combining with the displaced hydrogen and thereby eliminating it with less expenditure of energy than would be required to form bubbles. Oxygen also removes ferrous hydroxide from the reaction by converting it to ferric hydroxide. The removal of both reaction products, hydrogen and ferrous hydroxide, naturally accelerates the process of corrosion.

Differences in oxygen concentration of the water at different points on the surface of a specimen may be enough to cause severe corrosion. Iron dissolves anodically at points where the oxygen concentration is lowest, and hydrogen is deposited at the cathodic areas where the oxygen concentration is relatively high. The effect of these oxygen-concentration cells, and their importance in connection with pitting and other phenomena of corrosion, have been studied extensively by Evans. It has been suggested by Toporescu[1033] that surface-tension effects may stimulate corrosion in aqueous solutions.

Carbon dioxide frequently plays an important part in aqueous corrosion, accelerating rusting according to Evans[659] and Abegg,[914] but is usually secondary in importance to oxygen. Evans[777] accounted for the effect of carbon dioxide or weak organic acids on the ground that these materials accelerate the formation of soluble ferrous salts. Fujihara[610] expressed the same idea in a different way, *viz.*, that the main rôle of carbon dioxide is the removal of the film of ferrous hydroxide as fast as it is formed.

166. The Corrosion of Pure Iron in Pure Water.—The question whether theoretically pure and homogeneous iron would corrode in pure water was long a controversial subject. It was argued that a piece of pure metal, homogeneous and free from strains, could not corrode since there were no cathodic areas on which hydrogen could be liberated and no local couples to stimulate galvanic action. The unusual resistance to corrosion of Lambert's very pure iron[216,260,284] was frequently cited as evidence. Lambert's iron was prepared by electrolysis of a solution of purified ferric chloride, dissolving the deposited iron in nitric acid, recrystallizing the ferric nitrate, igniting the recrystallized nitrate to ferric oxide, and reducing the oxide with hydrogen to form metallic iron. Specimens were kept "in

contact with pure water and pure oxygen, under atmospheric pressure, for more than two years without showing any signs of corrosion or alteration of any kind."[260]   Pieces of the iron remained quite bright in the ferroxyl test.   Cold dilute sulphuric and nitric acids had very little visible action but cold dilute hydrochloric acid caused the slow evolution of bubbles of hydrogen, and the metal readily dissolved in all three acids on warming. It withstood the action of saturated solutions of copper sulphate or copper nitrate for an indefinite time at ordinary temperatures, without visible loss of metallic luster, but dissolved completely, depositing copper, when the temperature was raised to 100°C. (210°F.).

If pieces of this iron were subjected to mild local deformation by pressing with a pestle, the pieces so treated were decidedly inferior to untreated specimens in resistance to corrosion.   Pieces which had been immune to attack by water and oxygen showed signs of corrosion in less than 1 hour's immersion after being subjected to mild pressure, and the pressed metal rapidly developed anodic and cathodic areas in the ferroxyl test.

Iron prepared in an identical manner, except that platinum was used in place of the iridium electrodes and boats, corroded more readily, presumably on account of the presence of a trace of platinum in the iron.   Furthermore, iron prepared in a similar manner from ordinary ferric nitrate, even after 10 recrystallizations, corroded readily when exposed to water and oxygen. From all these results, Lambert concluded that pure iron will not undergo visible oxidation in contact with pure water and pure oxygen, but that a small trace of impurity, or the existence of strained areas in the metal, may suffice to cause oxidation under exactly the same conditions.   As Bancroft remarked,[545] Lambert made out an astonishingly good case for the non-corrodibility of homogeneous metal.   There was some justification for this belief, for

. . . since differences of homogeneity will tend to cause local voltaic cells and will therefore tend to cause corrosion, the natural corollary is that, *if other things are equal,* the most homogeneous metal will corrode the least rapidly.   This is absolutely sound, . . . *but the difficulty is to insure that all other things are equal.*

The authors have italicized the portions of this quotation which, as Bancroft pointed out, were usually overlooked by the proponents of the non-corrodibility of homogeneous metal.

Bancroft suggested that the non-corrodibility of Lambert's iron was probably due more to passivity than to true corrosion resistance. The destruction of corrosion resistance by the application of mild pressure to the specimens, and the behavior in acids and in solutions of copper salts, were phenomena which have been previously ascribed to passivity. The fact that passivity is readily developed in very pure irons—in fact, it is difficult to avoid—was discussed in connection with "pure" iron mirrors, for example those of Freundlich and his coworkers.[712]

As long ago as 1916, Stead[356] stated that on long etching of polished sections of any aggregation of iron crystals in dilute nitric acid, copper ammonium chloride, etc., the crystals with cube faces parallel to the surface were always the slowest to be attacked and stood out in bold relief above the surface of other crystals of different orientation. Hausser and Scholz[6654] experimented with single crystals of copper and of silver and found that preferential attack by different etchants occurred on different faces of a single-crystal ball specimen. They found that the cube faces of copper oxidized first and that nitric acid, which contained silver, attacked the cube edges, but that nitric acid, which contained mercury, or ammonia plus hydrogen peroxide attacked the rhombododecahedral faces. The idea that a homogeneous metal is subject to electrolytic corrosion as a result of varied orientation of the different grains definitely indicates that polycrystalline material is corrodible, even though it is chemically homogeneous. This belief was repeated by Stansfield[944] who further pointed out that differences in oxygen concentration can also initiate corrosion of a homogeneous metal. It appears therefore that a very pure metal is subject to corrosion, if it is polycrystalline, owing to the varied orientation of the exposed faces; and even if only a single face of a single crystal is exposed, corrosion may occur if there are local differences in oxygen concentration.

Bancroft[545] some years ago remarked that it was rather curious that the delusion that homogeneity was the most important variable should have taken hold of people so firmly. Speller[686] stated that from the standpoint of corrosion, homo-

geneity of a metal was not usually so important as external conditions; Richardson[421] concluded that "the production of an iron which will resist corrosion because of its purity is impossible of attainment"; and the results of Stead[356] and of Stansfield[944] demonstrate that even the purest and most homogeneous irons are subject to corrosion. However, some authors, for example Palmaer,[934] still insist that an absolutely pure metal with a homogeneous surface should not be dissolved by acids as the electromotive force is the same at all points. The arguments pro and con on this point were reviewed recently by Watts.[1036]

167. Corrosion of Commercially Pure Iron in Aqueous Solutions.—The various studies of the comparative corrodibilities of high-purity iron, such as electrolytic iron, and materials of commercial purity, such as Armco iron, wrought iron, and mild steel, indicate that all are subject to corrosion although not always to the same extent. Fujihara[661] rated electrolytic iron, Armco iron, and wrought iron in order of decreasing resistance to the mildly corrosive mixture of equal parts of ethyl alcohol and water. Fuller[662] found that in non-oxidizing solutions electrolytic iron was about three times as resistant as dead soft steel but in oxidizing media there was little, if any, difference. The behavior of electrolytic iron in $N/2$ K_2SO_4 solution was typical of that of mild steel and cast iron according to McAulay and Bastow.[846] Burgess and Engle[140] found that electrolytic iron in N H_2SO_4 lost weight at the same rate as did transformer iron, but less than a sample of a cutlery steel. In a comparison of electrolytic iron, wrought iron, and Armco iron Hatfield[470] found no difference in the corrodibilities in nitric acid, running water, intermittent immersion, steam at $100°C.$, sea water, and a variety of salt solutions. However, in hydrochloric acid and sulphuric acid electrolytic iron was superior in resistance to Armco, which in turn was superior to wrought iron; in certain organic acids the corrosion of electrolytic and Armco iron was about the same; but wrought iron was attacked more than the other two. Tiemann[1032] cited the experiments of Friend and of Heyn to show that, although absence of electrolytic couples in a very pure steel does retard the commencement of corrosion, it does not affect the rate of corrosion once the process has begun.

As a result of a series of extended investigations, Friend[330,713, 779,828,966] concluded that wrought iron and mild steel on the whole

suffered about alike in exposure to various aqueous solutions, as well as to the atmosphere. In some cases there was greater divergence between individual specimens in the same class than there was between the average results for different classes of material. Evans[659] agreed with Friend that there was no great difference between wrought iron and steel in resistance to corrosion; either one might be better for a particular purpose. Richardson[421] concluded that in submerged corrosion, external conditions overbalance composition in most cases in determining the course of corrosion. Friend[235] agreed with Richardson and extended the statement to include corrosion in general. Speller[686] found that the ordinary variations in commercial iron were of insignificant importance in underwater or underground corrosion, but in water containing free acids or acid forming compounds, or under alternate wet and dry conditions, composition was relatively a more important factor.

It has been shown that the rate of corrosion varies, among other conditions, with the hydrogen-ion concentration. Consequently, iron should corrode faster in acid solutions and slower in alkaline solutions than it does in neutral water. This is generally true although the rate of corrosion, particularly at first, is subject to the influence of other factors such as overvoltage and passivity. The extent of corrosion is influenced chiefly by the solubility of the salts of iron and by the formation of protective films. Corrosion in salt solutions is complicated by the effects of both anion and cation, in addition to all the other effects of concentration of salt and of hydrogen ions, passivity, overvoltage, and solubility.

In view of all the factors which may affect the rate and extent of corrosion it is not surprising that the results of corrosion tests are notoriously hard to duplicate. In addition, relatively few data are available for high-purity iron. For these reasons the data presented in the succeeding pages are intended to indicate, not to define, the approximate relative rates of corrosion of iron in different media. Many of them are of theoretical interest rather than of practical worth. The data on the corrosion of iron in mineral acids, for example, are included for their value in developing theories of corrosion and in showing the relative importance of changes in composition or in conditions of exposure,

not with any idea of suggesting that iron might be a useful container for such materials.

168. Data on Corrosion in Hydrochloric Acid.—Electrolytic iron dissolved rapidly in dilute hydrochloric acid according to Gray and Thompson[968] and to Evans[659] but only very slowly according to Tammann and Neubert.[948] Rohn's[685] "pure" iron lost 0.5 g. per sq. dm. per day in 10 per cent HCl at room temperature and 33.8 g. per sq. dm. in 1 hr. in hot 10 per cent acid. Lambert's iron[260] was attacked more readily by cold
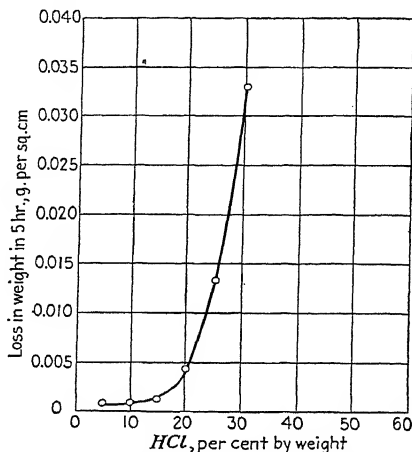
FIG. 67.—Effect of concentration of hydrochloric acid on attack on Armco iron. (*Endo.*[774])

dilute hydrochloric acid than by either nitric or sulphuric acid, and the attack was further increased by warming the solution, or by a slight change in composition of the metal. Hatfield[470] found that electrolytic iron lost 0.0814 g. per sq. cm. during 24 hr. in concentrated hydrochloric acid at 15°C. (60°F.).

Ingot iron lost 0.01 g. per sq. cm. per hr. in N HCl, but this rate of loss was increased 70-fold by the presence of platinum in contact with the iron (Evans[659]). Endo[774] found that the presence of oxygen increased the rate of solution 70-fold in 0.005 per cent HCl and 15-fold in 5.0 per cent HCl, in comparison with the same acids, oxygen-free. The effect of concentration of hydrochloric acid on the corrosion of Armco iron, according to

Endo, is shown in Fig. 67. The rate of corrosion of mild steel increased with increasing concentration of acid (Speller[686]) and proceeded over 15 times as fast in the presence of oxygen as in its absence (Evans[659]); in 10 per cent HCl the rate of corrosion of mild steel increased two or three times with each 10°C. rise in temperature between 40 and 80°C. (105 and 175°F.) (Calcott, Whetzel, and Whittaker[501]); the rate of solution of iron in hydrochloric acid increased with time, owing to increased porosity and consequently greater surface area as a result of corrosion (Rane and Prasad[626]).

The presence of chlorides of tin, chromium, or bismuth in 19 per cent HCl accelerated the attack of this solution on mild steel, according to Watts,[267] but the addition of sodium stannate, sodium chloride, or antimony sulphate retarded the attack. Rane and Prasad[626] found that the addition of alkaloids in amounts as low as 0.00033 g. per liter was remarkably effective in decreasing the rate of attack of N HCl on iron. In order of increasing effectiveness they listed brucine, strychnine, cinchonine, nicotine, codeine, cocaine, conine. These authors also discussed the inhibiting effect of additions of arsenious acid and agreed with the suggestion, previously offered, that the effect might be due to the protective action of a thin film of deposited arsenic. Warner[868] concluded that inhibitors of the organic type such as gelatine, quinoline, aniline, and bases from petroleum fractions or from coal-tar oils functioned by increasing the overvoltage required for the deposition of hydrogen. Gray and Thompson[968] found that nitriding electrolytic iron in molecular nitrogen supplied temporary protection against hydrochloric acid although similar treatment in ammonia increased the solubility 16 to 24 times over that of the untreated specimens.

169. Data on Corrosion in Nitric Acid.—Cold dilute nitric acid had very little visible action on Lambert's iron[260] but warming the acid, or a slight change in composition of the metal, resulted in increased corrosion. Hatfield's[470] electrolytic iron was "readily soluble" in HNO$_3$ of 1.20 sp. gr., losing 0.7165 g. per sq. cm. in 24 hr. Rohn's "pure" iron[685] lost 0.33 g. per sq. cm. in 2 hr. in 10 per cent HNO$_3$. Ingot iron lost 2.3 g. per sq. cm. per hr. in N HNO$_3$, and the presence of platinum in contact with the iron made very little difference in this rate, according to Evans.[659] Speller[686] found that the penetration of a mild steel

averaged 0.61 in. per year in 70 per cent HNO_3 and 1.82 in. per year in 1.2 per cent acid.

The effect of concentration of nitric acid in the attack on Armco iron, according to Endo,[774] is shown in Fig. 68. Thompson[690] found that the rate of attack on electrolytic iron increased to a maximum between 25 and 45 per cent of acid, by weight, and then dropped sharply with increasing concentration up to 68 per cent.
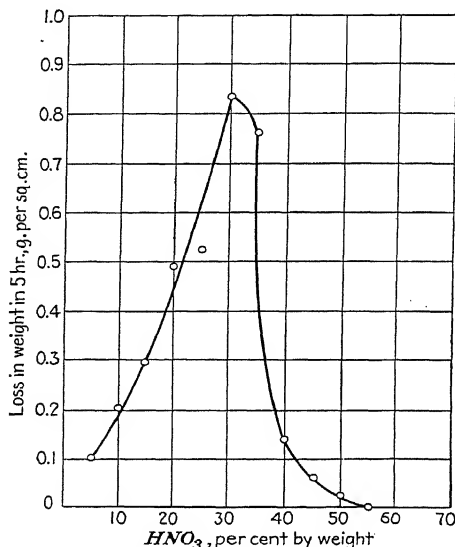
Fig. 68.—Effect of concentration of nitric acid on attack on Armco iron. (*Endo.*[774])

Evans[659] pointed out that the attack of nitric acid on iron was complicated as N_2, NH_3, N_2O, NO, and NO_2 might be produced, in proportions depending on the concentration of the acid, the degree of cold work, and the carbon content of the metal. Speller[686] observed that oxidizing acids such as nitric corroded relatively pure irons more rapidly than heterogeneous metals such as gray cast iron. The presence of oxygen slightly increased the attack of 1 per cent HNO_3 on Armco iron, but did not affect the rate of attack of 50 per cent acid, according to Endo.[774] Evans[659] stated that dilute nitric acid attacked iron readily but

concentrated nitric acid induced passivity; Endo[774] reported that nitric acid above 50 per cent hardly ever attacked iron.

170. Data on Corrosion in Sulphuric Acid.—In general terms, Evans[659] stated that iron liberates hydrogen from sulphuric acid, more rapidly for impure iron than for metal of higher purity. Speller[837] made the same statement and added that the corrosion of iron in sulphuric acid increased perhaps threefold for a 10° increase in temperature.
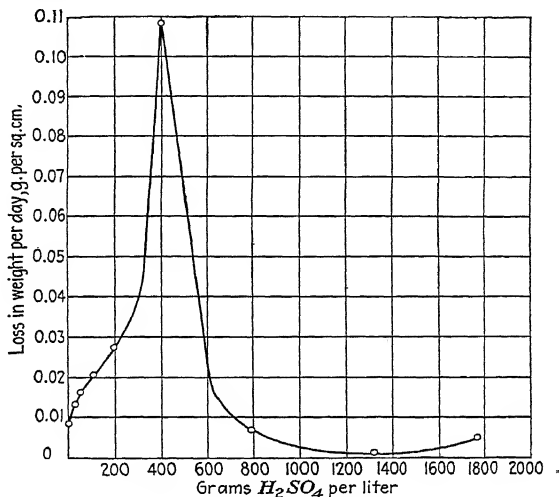
FIG. 69.—Effect of concentration of sulphuric acid on corrosion of electrolytic iron in intermittent immersion test. (*Fink and De Croly.*[827])

Cold dilute sulphuric acid had very little visible action on Lambert's iron,[260] but warming of the acid or a slight change in composition of the metal resulted in increased corrosion.

Electrolytic iron was slightly attacked by 10 per cent H_2SO_4 at 15°C. (60°F.), losing 0.0327 g. per sq. cm. in 24 hr., according to Hatfield;[470] Burgess and Engle's electrolytic iron,[140] heated to 1000°C. (1830°F.) to remove hydrogen, sustained an average loss of 0.0014 g. per sq. cm. per hr. during an 11-hr. exposure to normal sulphuric acid; Rohn's "pure" iron[685] lost 1.1 g. per sq. dm. in 24 hr. in 10 per cent H_2SO_4; an average grade of electrolytic iron lost 1.3 g. per sq. dm. in 1 hour's exposure to 20 per cent H_2SO_4;[643] the maximum corrosion rate for electro-

lytic iron subjected to intermittent immersion in sulphuric acid of different strengths was reached at an acid concentration of about 400 g. per liter, according to the results of Fink and de Croly,[827] reproduced in Fig. 69. In Burgess and Engle's experiments[140] electrolytic iron in normal sulphuric acid cor-
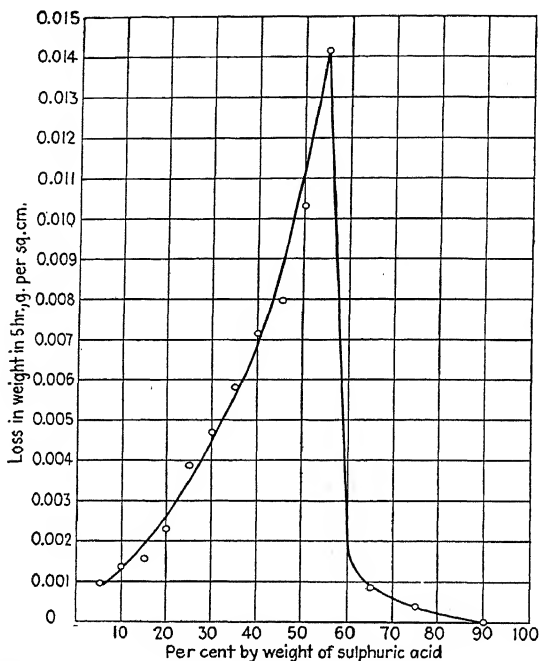
FIG. 70.—Effect of concentration of sulphuric acid on attack on Armco iron. (*Endo.*[774])

roded at the same rate as did transformer iron, but much slower than cast iron and plain carbon steel. In these experiments, electrolytic iron which had not been heated to remove hydrogen lost 10 times as much weight as did a similar piece from which the hydrogen had been removed. Stoughton[491] reported that in 22 hours' exposure to 5 per cent H_2SO_4, a sample of mild steel lost 4.25, and wrought iron 18.5, times as much weight as did electrolytic iron.

Ingot iron, according to Evans,[659] lost 0.05 g. per sq. cm. per hr. in N H_2SO_4, and lost 20 times as much when it was immersed in contact with platinum. Abegg's statement[914] that Armco iron corroded at a maximum rate in 55 per cent acid, with no loss in weight in 90 per cent acid during 5 hr., was based on Endo's results,[774] shown in Fig. 70. The general shape of this curve resembles that of the curve for electrolytic iron, Fig. 69, but the two curves are not directly comparable, one being based on continuous immersion of Armco iron, the other on intermittent immersion of electrolytic iron.

Endo found that the presence or absence of oxygen did not appreciably affect the corrosion of Armco iron in 95 per cent H_2SO_4, but did affect results in more dilute acids; for example, the presence of oxygen increased the rate of attack 14 times in 5 per cent acid. Whitman and Russell[643] reported that the corrosion of mild steel in concentrated sulphuric acid might be greater in the absence than in the presence of dissolved oxygen, due to the passivifying action of dissolved oxygen. These authors also called attention to the effect of agitation; in 80 to 100 per cent acid the corrosion of mild steel was slight when there was no agitation; in concentrations above 90 per cent the rate of corrosion was markedly increased by increasing the velocity, probably due to the removal or prevention of formation of surface films.

Mechanical stress increased the rate of solution of steels of varying carbon contents, according to Endo.[776] In concentrated commercial acid mild steel corroded steadily over periods up to 2500 hr. and in oleum at 20 to 30°C. (68 to 86°F.) wrought iron corroded at the rate of 0.003 in. penetration per month.[501]

In general, the corrosion of iron in sulphuric acid was stimulated by the presence of various salts of copper and silver according to Watts and Knapp,[455] but the addition of salts of tin or arsenic decreased the corrosive attack of sulphuric acid on mild steel.[267] The presence of aniline in 10 per cent H_2SO_4 increased the hydrogen overvoltage and consequently decreased corrosion, according to Knowlton.[789] Warner[868] also ascribed to increased overvoltage the inhibiting action of small amounts of aniline, quinoline, petroleum bases, coal tar bases, and gelatine on the corrosion of low-carbon sheet iron in molal sulphuric acid.

171. Data on Corrosion in Phosphoric and Acetic Acids.— "Pure" iron lost 0.27 g. per sq. dm. in 24 hours' exposure to 10 per cent H_3PO_4, according to Rohn,[685] and Portevin and Sanfourche[936] reported that iron of higher purity than industrial was attacked by various concentrations of phosphoric acid. Abegg[914] concluded that phosphoric acid dissolved very pure iron to some extent but that iron phosphates tended to form protecting films.

"Pure" iron, according to Rohn,[685] lost 0.14 g. per sq. dm. in 24 hr. in 10 per cent acetic acid. Speller[686] reported that mild steel in acetic acid, in the presence of oxygen, was corroded at about the same rate (approximately 0.5 in. penetration per year) in both 6 per cent and glacial acetic acid.

172. Data on Corrosion in Acids in General.—Contact with another metal more noble than iron increases enormously the rate of solution in acids. Increased motion increases the rate of corrosion[422,626] and the presence of oxidizing agents frequently stimulates corrosion since the oxides of most metals are soluble in acids.[659] However, the stimulating effect of oxidizing agents is not so important with oxidizing as with non-oxidizing acids.[643] The presence of alcohol or any other material which interferes with dissociation lessens corrosion, and in strongly oxidizing acids such as nitric, chromic, chloric, and iodic acids solution is complicated by passivity phenomena.[914]

173. Corrosion in Alkaline Solutions.—Corrosion in alkaline solutions and corrosion in acids differ only in degree, and the effect of alkalinity probably depends mainly on decreased solubility of the hydroxides, according to Speller.[686] Evans[659] also believed that the reduction in solubility of ferrous hydroxide was responsible for the easy passivity of electrolytic iron in alkaline solutions. Evans pointed out that iron was appreciably attacked by a hot concentrated solution of caustic soda and was embrittled, possibly through hydrogen penetration, as a result of immersion in hot alkaline solutions. The caustic embrittlement of commercial iron, such as boiler plate, is well known.

In some experiments of Friend[235] strips of "pure" iron were kept in sealed tubes, in contact with air and dilute ammonium hydroxide, for several years without the slightest change in appearance being observed. The same author subsequently reported[467] that the purer forms of iron remained unattacked

by solutions of hydrogen peroxide in dilute sodium or ammonium hydroxides, although oxygen was liberated from the peroxide.

The following results of Friend[235] showed that high-purity iron, in the form of foil, was not damaged by immersion at room temperature in solutions of potassium hydroxide contained in open beakers:

KOH, g. per liter	Time, days	Loss, g.
0.0	28	0.0685
2.8	28	0.0000
28.	28	0.0001
168.	28	0.0003
Saturated	21	0.0002

Similar conclusions regarding solutions of calcium hydroxide and sodium hydroxide were drawn by Friend[235] from the results of 22-day-exposure tests by Heyn and Bauer:

Ca(OH)$_2$, g. per liter	Loss, g.	NaOH, g. per liter	Loss, g.
0.0	0.0646	0.0	0.0653
0.88	0.0000	10	0.0002
1.78 (saturated)	0.0000	100	0.0005
		saturated	0.0002

174. Corrosion in Salt Solutions.—Results of corrosion tests in salt solutions are unusually variable even for corrosion tests. The action of Lambert's[260] iron in solutions of alkali salts, in contact with air, was irregular. The metal corroded readily in a normal solution of sodium chloride, but sulphates and nitrates were less active than chlorides. If the metal was free from strains, it withstood attack by saturated solutions of copper salts, at ordinary temperatures, but dissolved completely if the temperature was raised to 100°C. (210°F.).

The effect of dissolved salts may be intimately related to their effect on the solubility of the corrosion products, according to Whitman[642,644] and Evans.[659] The latter called attention

to the fact that rusting of iron in neutral solutions was accelerated by the presence of chlorides and was retarded by alkalies and by chromates.   Chlorides in solution were particularly active in destroying passivity, and retained chlorides presumably were responsible for the rapid rusting of electrolytic iron from chloride baths as compared to similar iron from sulphate baths. Speller[686] concluded that magnesium chloride was the most harmful component of sea water used in marine boilers and that its objectionable effects resulted from a cyclic hydrolysis which liberated hydrochloric acid.

Evans[659] found that iron was attacked less rapidly by drops of pure water than by drops of solutions of potassium chloride, nitrate, or sulphate.   On the other hand, Friend and Brown[238] concluded that between 13 and 32°C. (55 and 90°F.), sodium chloride solutions of all concentrations exerted less corrosive action on iron foil than did fresh water at the same temperature. At 13°C. (55°F.) sea water and fresh water were the same in corrosive action, but diluted sea water was more corrosive than either.[659]   In his book, Friend[235] recorded that solutions of sodium chloride at room temperature and in the absence of air exerted no appreciable action on "pure" iron in 17 days.   In an intermittent immersion test in 5 per cent NaCl solution, Fink and de Croly[827] found that electrolytic iron lost 0.461 g. per sq. dm. per day.   Richardson[421] found that a 10 per cent solution of sodium chloride at rest was twice as corrosive as pure water to Armco iron, and the rate of attack was increased fourfold by agitation.

The mechanism of corrosion of electrolytic iron in solutions of potassium chloride and sulphate was studied in detail by Evans.[825]   Heyn and Bauer seem to have been the first to call attention to the fact that the rate of corrosive attack does not vary directly with the concentration of salt solutions.   Their conclusions regarding critical concentrations and varying rates of corrosion were substantiated by Friend and Brown[237] and by Endo,[774] working with a variety of chlorides, nitrates, sulphates, alums, chromates, etc.   Endo found that for solutions of non-oxidizing salts the effect of adding oxygen became greater with increasing concentration below 0.1 g. molecule, but in solutions of oxidizing salts such as potassium nitrate the effect of oxygen was almost constant, independent of concentration of the salt.

A study of the influence of added salts on the rate of corrosion of iron in salt solutions was reported recently by Tödt.[1072]

Ammonium salts of mineral acids are remarkably corrosive, particularly ammonium nitrate which probably contributed to the corrosive qualities of rain water, according to Friend.[235] These salts probably hydrolyze to liberate free acids. Pollitt[576] agreed that the corrosive action of rain water was due to the presence of dissolved substances, including oxygen.

Calcium or magnesium salts in natural waters may be either beneficial or detrimental in their effect on corrosion. The effect of the presence of magnesium chloride in sea water has been mentioned. Evans[777] pointed out that the rust produced by hard waters contained calcium and magnesium compounds and obstructed diffusion of oxygen to the metal, thereby reducing the rate of corrosion. The presence of magnesium sulphate at ordinary temperatures always reduced the rate of corrosion of half immersed specimens.[777] On the other hand, Speller[450] cited the fact that Great Lakes water with about 8 grains of calcium carbonate per gallon was very much more corrosive to iron than was New York City water containing 1 or 2 grains of carbonates, both having about the same amount of dissolved oxygen. A recent report[1022] described the study of the corrosion of Armco iron under carefully controlled conditions, in a relatively hard tap water in which the rust, formed on the specimens, contained an appreciable quantity of calcium carbonate.

The catalytic action of soluble salts of iron on progressive rusting was discussed by McCulloch,[677] and Worth[460] reported a case of unusual corrosion, in a steam boiler, which was finally traced to the presence of soluble iron bicarbonate in the water.

175. Miscellaneous Corrosive Agents.—Exposure to sunlight increases aqueous corrosion of iron. Endo[774] found that Armco iron, in distilled water, was definitely corroded to a greater extent when exposed to the sunlight, in comparison with experiments conducted in the shade.

Iron is subject to corrosion by many solutions aside from the ordinary acids and salts. For example, Kutter[841] found that iron was strongly corroded by both beer and wort, and Winkelmann[754] reported that iron was corroded by various fungicide solutions particularly those of mercury. It has been

reported[1043] that huckleberry swamp water, which is high in organic acids, is unusually corrosive to structural iron.

176. Summary of Corrosion in Aqueous Solutions.—Even the purest iron dissolves to a slight extent in pure water in the absence of oxygen and rusts in pure water in the presence of oxygen. In general, iron is subject to corrosion in aqueous solutions of acids, alkalies, and salts. The rate and extent of corrosion vary with a number of factors including hydrogen-ion concentration, presence of oxygen, agitation, temperature, and nature and concentration of the solution. Some degree of protection may result from passivity or from the formation of protective films but these factors, and the effect of purity and homogeneity in the metal, are usually of slight importance in submerged corrosion.

D. UNDERGROUND CORROSION

No information has been found on the subject of underground corrosion of high-purity iron. The results obtained in an extended investigation by the National Bureau of Standards[1061] are probably typical of underground corrosion tests of commercial irons and steels.

Underground corrosion combines factors of atmospheric and underwater corrosion and introduces some new ones, such as electrolysis from stray currents. Attack is usually accompanied by marked pitting. The amount of dissolved oxygen varies widely but is usually rather limited. Ordinary differences in composition of the metal are definitely less important than differences in locality and nature of the soil (Tiemann,[1032] Speller,[686] Logan, Ewing, and Yeomans[794]).

The reports of the National Bureau of Standards' investigation[287,794,843,929,1016,1061] indicate that, in the presence of so many variables, the rate of corrosion of any metal cannot be accurately expressed by a single figure or group of figures; that current density, concentration cells, moisture, and chemicals in the soil have marked effects; temperature variation and depth of burial have no particular effect; the effect of oxygen is particularly marked in affecting the end products of corrosion; variation in composition is relatively unimportant.

Ferrous materials are subject to corrosion underground. If high-purity iron were similarly exposed, it too would probably

corrode, especially as the conditions of underground exposure are not conducive to the development of passivity.

E. EFFECT OF IMPURITIES AND ADDED ELEMENTS ON CORROSION OF IRON

In this discussion of the effect of other elements on the corrosion of iron, consideration has been limited, in general, to amounts which might be considered as impurities rather than as alloys of iron. However, consideration of some data from the field of alloys of iron necessarily has been included, as have data for commercial forms of iron. The discussion is given according to the alphabetical order of the elements.

177. Aluminum.—Aluminum readily enters into solid solution in iron.[802] Data on the effect of aluminum on the corrosion of iron are limited; Pollitt[576] reported that less than 1 per cent of aluminum in "pure" iron did not change the corrosion rate; Burgess and Aston[274] found that 1 per cent or less of aluminum decreased the rate of corrosion of electrolytic iron in 20 per cent H_2SO_4 but was without effect in atmospheric corrosion.

Limited data indicate that small amounts of aluminum do not affect the corrosion of iron to an appreciable extent.

178. Arsenic.—Alloys of electrolytic iron and from 0.292 to 3.562 per cent arsenic were prepared by Burgess and Aston.[274] The presence of small amounts of arsenic did not affect the rate of atmospheric corrosion to an appreciable extent but did improve the resistance to 20 per cent H_2SO_4. Pollitt[576] stated that conclusive evidence regarding the effect of arsenic on corrosion was not available, and called attention to the fact that the arsenic content of steel usually is very low. The experiments of Heyn and Bauer, showing that iron suffered from increased attack by 1 per cent H_2SO_4 after being heated in arsine, were cited by Friend,[235] with the comment that the product of this treatment was hardly an arsenical alloy.

The presence of arsenic salts in solution reduced the corrosion of iron in dilute sulphuric acid, possibly owing to high overvoltage of hydrogen on a deposited film of arsenic. It failed to protect iron from corrosion by an acid solution of ferric chloride, which corrodes iron without the evolution of hydrogen.[659]

The amounts of arsenic ordinarily present in iron or steel probably are without effect on corrosion.

179. Carbon.—Very little carbon can be retained in solid solution in alpha iron at room temperature. Consequently, the presence of carbon usually means the presence of another phase with an increase in tendency to corrode. The importance of the state of combination of the carbon, in affecting the rate of solution, was pointed out by Endo,[775] Evans,[659] Pollitt,[576] and Abegg;[914] Friend[235] confirmed the conclusion of Heyn and Bauer, that a completely troostitic structure was least resistant to corrosion. Pollitt[576] reported that the corrodibility of annealed steels increased with increasing carbon up to about
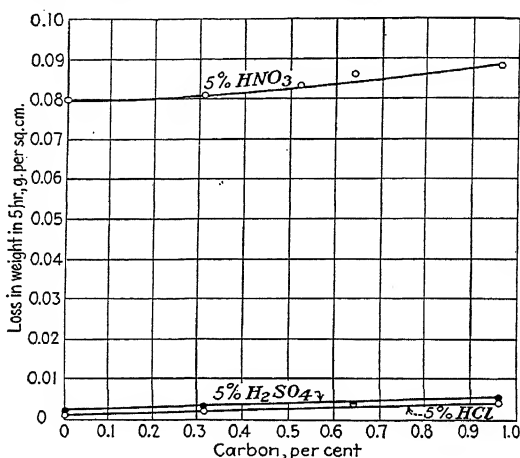
Fig. 71.—Effect of carbon on corrosion of Swedish iron in acids. (*Endo.*[775])

0.89 per cent, but that the corrodibility of quenched and tempered steels did not vary with the carbon content.

The corrodibility of iron or steel in sea water and in tap water increased with increasing carbon content to a maximum near 0.9 per cent according to Friend,[235,508] but Evans[659] found this increase to be slight, and Speller[686] considered the increase due to carbon, within the range of carbon content of structural steels, as comparatively unimportant in immersion under water.

Carbon in amounts under 0.20 per cent had little influence on the corrodibility of iron;[1032] carbon between 0.1 and 0.25 per cent did not affect the rate of solution of electrolytic iron in hydrochloric acid, but above 0.25 per cent the attack increased

slowly with increasing carbon, up to about 0.9 per cent.[948] Evans[659] believed that the rate of attack of iron by dilute acids increased with increasing carbon up to about 0.9 per cent, but Aitchison[323] reported that variation of the carbon from 0.07 to 1.46 per cent produced irregular variations in the corrosion in dilute sulphuric acid and in sodium chloride solutions.

The results of Endo,[775] presented in Fig. 71, show that increasing carbon, up to 1.0 per cent, increased slightly the rate of corrosion of a Swedish iron which was exposed for 5 hr. in 5 per cent HNO_3 but that the increase was hardly noticeable in 5 per cent HCl or H_2SO_4. This Swedish iron contained 0.08 per cent manganese, 0.09 per cent silicon, 0.024 per cent phosphorus, and 0.0065 per cent sulphur.

Apparently, small amounts of carbon, 0.2 per cent or less, are of negligible importance to the corrodibility of iron. Larger amounts increase the tendency to corrode, the extent of the increase being affected by the state of combination of the carbon. Carbon may affect the influence of other elements, such as manganese, on corrosion.

180. Chromium.—Information regarding the effect of small amounts of chromium on the corrosion of iron is limited. Chromium tended to retard corrosion in neutral solutions, according to Friend.[508] Hatfield[470] reported that an increase of chromium from 0.14 to 0.5 per cent in a 3 per cent nickel steel decreased corrosion in hydrochloric acid and sulphuric acid, and particularly in nitric acid. Guertler and Ackermann[782] found that the first additions of chromium had no noticeable effect on the attack by hydrochloric acid but slightly increased the attack by dilute sulphuric acid. Two per cent chromium increased the rate of solution of Endo's Swedish steel[775] in 5 per cent HCl and 5 per cent H_2SO_4 but decreased the attack of 5 per cent HNO_3. Two per cent chromium in iron slightly increased corrosion in 3 per cent NaCl, according to Aitchison.[323]

181. Cobalt.—One per cent cobalt decreased the corrosion of a readily corrodible electrolytic iron in atmospheric exposure and in 20 per cent H_2SO_4.[274] Two per cent increased corrosion in 5 per cent HCl and 5 per cent H_2SO_4 but decreased corrosion in 5 per cent HNO_3, according to Endo.[775] On the other hand, Aitchison[323] reported that 2 per cent cobalt produced some benefit on the corrosion rate in dilute sulphuric acid and

exerted no effect in 3 per cent NaCl.   Larger amounts of cobalt apparently slightly decreased the corrosion rate in the atmosphere, in sea water, and in tap water, but the effect was less than that of equal amounts of nickel.[576,686,1032]

Small amounts of cobalt may be slightly beneficial in their effect on the corrosion of iron in the atmosphere and in mildly corrosive aqueous solutions.   In acid solutions the presence of small amounts of cobalt appears to be detrimental more often than beneficial.

182. Copper.—The effect of small copper contents on the corrodibility of ferrous materials has occasioned more discussion than that of any other element.[273,428,432,469]   The results of extensive investigations of the subject, both in this country and abroad, are discussed in detail by Gregg and Daniloff[1055] in another volume of this series of monographs; the following brief summary is quoted largely from their conclusions.

The use of copper as an alloying element in steel does not "solve the corrosion problem" or produce a "rustless steel." The order of improvement produced by copper is a relatively small one compared with that obtained by the use of large amounts of chromium in the so-called "stainless steels."   Moreover, the improvement in corrosion resistance caused by copper is obtained only under some, but not all, corrosive conditions. Nevertheless, the prolongation of the life of a steel article under atmospheric exposure by approximately 50 per cent and at the slight cost of adding a few tenths of 1 per cent of copper is of marked economic advantage.

The resistance of ferrous materials to atmospheric corrosion increases rapidly as the copper content increases to 0.25 per cent, but further increase has little influence on the rate of corrosion.   The presence of copper does not prevent initial corrosion of the surface but the surface coating, once it is formed, furnishes better protection to the underlying metal than is afforded by the coating on copper-free material.   The protective action is due to the continuity and adherence of the film which forms on copper-bearing iron or steel; the action may become injurious if the film is not continuous over the entire surface.

The results of tests of the influence of copper in underwater corrosion are not in good agreement, particularly for sea-water tests.   In general, the influence of copper is considerably weaker

than in atmospheric tests; the results apparently may be influenced by the external test conditions in such a way as to deflect the conclusion to one side or the other, *i.e.*, to condemn copper as a harmful element, or to claim for it beneficial effects.

In underground corrosion the effect of external factors far exceeds the influence of small variations in the content of common elements, including copper, usually present or alloyed with iron or steel.

183. Gold.—Any amount of gold between 0.01 and 2.0 per cent markedly increased the corrosion of electrolytic iron in 3N H_2SO_4, according to Tammann and Neubert.[948] The presence of a noble metal such as gold would be expected to increase the corrosion of iron, unless the gold were present in solid solution.

184. Hydrogen.—The presence of hydrogen in electrolytic iron increased the rate of attack by acids, but the hydrogen could be removed by heating, according to Burgess and Engle.[140] As Speller[686] pointed out, practically nothing is known from the corrosion standpoint of the effect of gaseous elements dissolved in the metal.

185. Inclusions.—Through the use of the ferroxyl indicator, Cobb[232] found that iron was definitely anodic to most of its impurities, including phosphide, sulphide, carbide, oxide, and silicate of iron, and particularly to graphite. Iron also was anodic to all of the ferroalloys tested, except ferromanganese. These results apparently showed that the presence of any impurity as a separate phase would tend to increase the corrosion of the specimen. However, it must be remembered that the reliability of the ferroxyl indicator has been questioned, for example by Walker[168] and by Bancroft.[545]

Sulphide inclusions have long been considered objectionable on the ground that they stimulate galvanic activity and, when oxidized, form sulphurous or sulphuric acid.[235] However, recent work by Homer[972] and by Tronstad and Sejersted[1034] indicated that not all sulphide inclusions were equally objectionable and that a large portion of the sulphide particles were nearly or completely inert. Homer reported that in distilled water, tap water, and in some salt solutions, corrosion always began adjacent to certain sulphide inclusions or embedded scale. Silica and alumina inclusions apparently were inert. Corrosion in sodium chloride solutions and in sea water apparently was

independent of inclusions other than embedded scale. The addition of sodium carbonate to certain aqueous solutions localized the corrosive attack at inclusions.

Cinder and slag inclusions in small amounts had no effect on the atmospheric corrosion of wrought iron, although a beneficial effect was evident if the amount of inclusions exceeded 2 per cent, according to Speller.[686] Friend and Thorneycroft[608] believed that the beneficial effect of slag inclusions in wrought iron was probably due to the fact that corrosion pits stopped when they encountered a slag inclusion but continued indefinitely in the absence of slag.

A secondary but important effect of inclusions on the rate of corrosion was pointed out by Evans.[659] There are likely to be cavities where inclusions occur, partly owing to the difference in contraction during cooling, partly to the low adhesional forces between metallic and non-metallic materials, and partly (in worked metals) to the absence of malleability in some types of inclusions. Corrosion is prone to begin and to persist in these cavities to which oxygen has slight access, provided that there are adjacent areas to which oxygen can penetrate freely. Corrosive attack on iron frequently follows slag lines.

Apparently, non-metallic inclusions are objectionable from a corrosion standpoint for two reasons; first, some of them stimulate galvanic activity, and second, even chemically inert inclusions may be accompanied by minute cracks and cavities in which the objectionable pitting form of corrosion can develop.

186. Iron Oxides (Rust).—In exposure to the atmosphere or to intermittent immersion tests, the first product of the corrosion of iron is ferrous oxide or hydroxide which is subsequently oxidized to the corresponding ferric compounds. The outer surface of a film of rust therefore is rich in ferric iron, the inner surface is rich in ferrous iron.[1068] Soderberg[943] showed that similar reactions occur in some cases of immersed corrosion. Rust was considered by Friend[235] to be a powerful stimulant to corrosion; Fe_3O_4, produced by heating iron in air at elevated temperatures, being less active and less adherent than Fe_2O_3.

A continuous film of adherent rust may supply an appreciable amount of protection to the underlying metal. For example, Speller[686] found that the removal of mill scale from old wrought irons was followed by prompt rusting of the exposed areas.

On the other hand, a non-continuous film of rust may promote corrosion. Aston[345] was apparently the first to call attention to the fact that rust and other inert substances which exclude oxygen from the surface render the underlying iron anodic and the areas to which oxygen has freer access cathodic. Evans[659] pointed out that the presence of rust may further corrosion in either of two ways; a compact layer of dried rust often tends to protect the metal just below it and to promote attack upon the adjacent areas; flocculent wet rust is usually favorable to the continued eating away of the metal underneath it. Vernon[1035] reported that rusting can occur at humidities below the dew point, provided ferric hydroxide is present on the iron. His explanation is that, for humidities of more than 65 per cent, the capillaries of the ferric hydroxide gel fill with water as a result of capillary attraction, and this water then is free to pass to the surface of the metal. If the humidity is less than 65 per cent, water forms in the capillaries but does not fill them and consequently is not available to cause rusting.

Rust which completely covers the surface of iron with a continuous film may afford some measure of protection to the underlying metal, but rust which covers only a portion of the surface promotes corrosion, not only of the adjacent bare metal but in some cases of the metal already covered by the rust.

187. Lead.—The addition of 0.06 per cent of lead to Burgess and Aston's electrolytic iron improved the resistance to atmospheric corrosion but had no effect on the corrosion in 20 per cent H_2SO_4.[274]

188. Manganese.—Manganese was formerly considered objectionable from the standpoint of resistance to corrosion,[235] but the decrease in resistance to corrosion may have been due to manganese sulphide,[209,352,576,686] or to manganese oxide,[686] rather than to metallic manganese. The effects of manganese are influenced by the carbon content.[775] Beneficial effects of manganese were reported by Tiemann[1032] for corrosion in general; Burgess and Aston[274] reported that additions of manganese, even in small amounts, decreased the corrosion of electrolytic iron in the atmosphere or in 20 per cent H_2SO_4; Hadfield and Friend[352] found that manganese up to 2 per cent decreased corrosion in tap water and sea water but increased the corrosion in dilute sulphuric acid; Friend[503] found that increasing

the manganese content from 0.1 to 0.9 per cent did not greatly affect corrosion in sea water but increased appreciably the corrosion in dilute sulphuric acid. Two per cent manganese had very little effect on corrosion in 5 per cent HCl, H_2SO_4, and HNO_3, according to Endo,[775] but Utida and Saito[638] found that an increase of manganese from 0.95 to 4.36 per cent increased corrosion in 10 per cent HCl, HNO_3, and H_2SO_4.

Manganese in the amounts usually encountered did not affect corrosion;[501] in the absence of sulphur it was not objectionable;[352] up to 0.5 per cent it had no definite effect in the absence of manganese oxide and sulphide, but when manganese was associated with unusually high sulphur the rate of corrosion was accelerated, particularly in acid media and in the air.[686]

The effect of manganese up to 0.5 per cent is probably not important in the corrosion of iron. In the presence of sulphur, carbon, or oxygen the effect of manganese is not beneficial.

189. Mercury.—The effect of amalgamation of iron is similar to that of zinc but is less permanent. Evans[659] found that amalgamated iron withstood attack by 15 per cent H_2SO_4 for a day or two but the protective effect may vanish quite suddenly, probably because mercury spontaneously gathers together in globules.

190. Molybdenum.—More than 1 per cent molybdenum exerted a harmful influence on the corrosion rate in intermittent immersion tests but, in amounts up to 4 per cent, molybdenum was without appreciable effect on corrosion in tap water, salt solutions, and dilute sulphuric acid, according to Speller.[686] However, Friend and Marshall,[302] Aitchison,[322] and Endo[775] found that 2, 3, or 4 per cent molybdenum increased the rate of attack in dilute acids, in salt solutions, and in intermittent immersion tests. In another volume of this series of monographs, Gregg[969] pointed out that molybdenum lies between tungsten and chromium in the periodic arrangement of the elements but is less noble than tungsten and does not become passive like chromium; consequently, it would not be expected to produce a marked increase in the resistance to chemical attack. However, Eisenkolb[1051] recently reported that the beneficial effect of 0.33 per cent copper, in resistance to atmospheric corrosion, is further increased by the addition of 0.08 per cent molybdenum.

191. Nickel.—About 1 per cent nickel was beneficial in atmospheric corrosion of iron, according to Pollitt[576] and to Burgess and Aston.[274] Tiemann[1032] concluded that in atmospheric corrosion the effect of nickel was similar to that of copper, except that probably more nickel was required. Friend[235] found that 0.2 per cent nickel was without effect in the corrosion of steel.

In acid corrosion, Pollitt[576] and Burgess and Aston[274] found that 1 per cent nickel was effective. The first additions lowered the rate of solution of iron in dilute nitric and sulphuric acids but did not affect the rate of solution in hydrochloric acid, according to Guertler and Ackermann.[782] However, Endo[775] reported that 2 per cent increased the rate of solution in dilute hydrochloric and sulphuric acids but decreased it in dilute nitric acid, and Utida and Saito[638] concluded that nickel decreased corrosion in all three acids. Aitchison[323] found that less than 3 per cent of nickel increased corrosion in 3 per cent NaCl and in dilute sulphuric acid, but Friend[508] reported possibly a slight benefit from 2 to 3 per cent.

Nickel does not produce pronounced resistance to corrosion in iron although the presence of small amounts is of some benefit in atmospheric corrosion. Speller[686] concluded that a minimum of about 3 per cent was necessary to produce a definite effect, and Friend[508] pointed out that even Invar is subject to attack in rather mild corrosive media.

192. Nitrogen.—There is practically nothing known, from the corrosion standpoint, of the effect of the presence of gaseous elements dissolved in the metal, according to Speller.[686] Aupperle[496] found some evidence that atmospheric corrosion increased directly in proportion to the nitrogen content.

Nitriding processes, which consist in subjecting steel of the proper composition to the action of a nitrogeneous medium (usually ammonia gas) at elevated temperatures, produce a nitrogen-rich surface layer which, in addition to wear resistance, surface hardness, and retention of hardness at elevated temperatures, exhibits resistance to certain types of corrosion. The nitrogen content of a nitrided case may be several per cent in contrast to the few thousandths, or at most one or two hundredths, of 1 per cent of nitrogen which is present in ordinary steel. According to Homerberg[1006] nitrided steel is resistant to

alkali, atmosphere, crude oil, natural gas combustion products, tap water, still salt water, and to oxidation and corrosion in superheated steam; is slightly attacked in aerated salt water and in intermittent exposure to salt water; is not adapted for use in mineral acids such as sulphuric and hydrochloric. Homerberg emphasized the point that the maximum resistance to corrosion is shown by the outermost layers of the nitrided case. Consequently, nitrided specimens should not be ground after the nitriding operation if maximum resistance to corrosion is desired.

193. Phosphorus.—Phosphorus, particularly if present in large amounts, has been considered objectionable from the standpoint of corrosion resistance.[209,235,501] In Endo's experiments[775] phosphorus up to about 1 per cent seemed to increase the rate of solution of Swedish steel in 5 per cent HCl and 5 per cent H_2SO_4 but decreased the solubility in 5 per cent HNO_3. Other investigators, for example Speller,[686] concluded that phosphorus had very little influence on corrosion. It was reported recently[1034] that phosphorus, between 0.011 and 0.03 per cent, being present mainly in solid solution, produced no appreciable effect on corrosion in 2N NaCl solution. Tiemann[1032] reported that 0.10 per cent phosphorus may increase the resistance to atmospheric corrosion, and Friend[235] found that additions of phosphorus, up to 1 per cent, decreased corrosion in sea water. Pollitt[576] concluded that phosphorus appeared to be beneficial rather than otherwise but called attention to the harmful effects of segregation. A reference has been encountered to a French patent (I. G. Farbenindustrie A. G., French Patent 704,854, November 3, 1930) for preservation of iron from rusting based on heating to between 300 and 900°C. (570 and 1650°F.) for about 24 hr. in a non-oxidizing atmosphere which contained either elemental phosphorus or a compound such as phosphine.

Phosphorus, formerly considered objectionable, may be beneficial in some cases. Amounts of phosphorus retained in solid solution in iron probably have little, if any, effect on corrosion.

194. Selenium.—A small amount (0.017 per cent) of selenium decreased corrosion in 20 per cent H_2SO_4 but increased atmospheric corrosion of Burgess and Aston's electrolytic iron.[274]

195. Silicon.—A silicon content of 0.233 per cent slightly increased corrosion in 20 per cent H_2SO_4 but had no effect on

atmospheric corrosion of Burgess and Aston's electrolytic iron.[274] Endo[775] found that 2 per cent silicon in Swedish steel gave a minimum rate of solution in 5 per cent HCl and 5 per cent H_2SO_4, but had little effect in 5 per cent HNO_3. Evans[659] quoted these and other results and concluded that silicon decreased corrosion in hydrochloric, nitric, and sulphuric acids. Small amounts of silicon definitely improved the resistance of iron exposed in air at 1100°C. (2010°F.), according to Utida and Saito.[638]
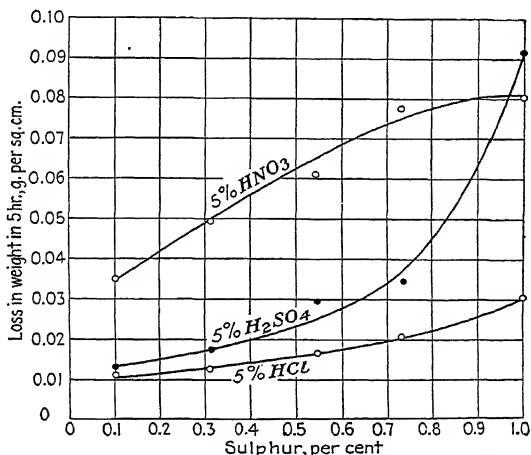
Fig. 72.—Effect of sulphur on corrosion of Swedish iron in acids. (*Endo.*[775])

Less than 0.10 per cent silicon had no effect on corrosion according to Tiemann,[1032] but Pollitt[576] believed that less than 2.5 per cent silicon may actually increase corrosion and that the normal silicon content of steel probably had little effect, although that effect was more likely to be bad than good. Speller's results[686] indicated that corrosion in immersion tests was not increased by silicon up to 3 per cent. Kowalke[380] reported that alloys of electrolytic iron with less than 5 per cent silicon were readily attacked by dilute sulphuric, hydrochloric, nitric, acetic, and citric acids. The conclusion reached in the recent monograph on "The Alloys of Iron and Silicon"[1000] is that the effects of silicon, below about 15 per cent, are variable and not important in corrosion.

Apparently definite beneficial effects of silicon, in resistance to corrosion, are obtained only from high silicon contents.

196. Silver.—Silver contents between 0.28 and 0.69 per cent had very little effect on the rate of corrosion of Burgess and Aston's electrolytic iron, in the atmosphere and in 20 per cent H_2SO_4.[274]

197. Sulphur.—A number of investigators agreed that sulphur, in appreciable amounts, stimulated corrosion, both atmospheric and in acids[235,501,659,775,1032,1034] and that sulphide inclusions were particularly effective in stimulating localized corrosion through galvanic action.[235,576,950,972,1034] The results obtained by Endo[775] for the effect of sulphur on the corrosion in 5 hr. of Swedish iron in dilute acids are shown in Fig. 72. The corrosion rate in the atmosphere increased directly with the sulphur content, according to Tiemann,[1032] and in general corrosion, according to Pollitt.[576] Other authorities[501] stated that sulphur may increase corrosion if present in sufficiently large amounts. Speller[686] believed that the harmless percentage of sulphur was uncertain and was influenced by other constituents, but that moderate amounts (perhaps 0.06 per cent) had very little influence on atmospheric or neutral-water corrosion, although the effect might become noticeable in acid waters. The bad influence of sulphur may sometimes be neutralized by the presence of copper.

The presence of high sulphur, and particularly of sulphide inclusions, increases the corrosion of iron. The effect of low sulphur contents, 0.1 per cent or less, has not been definitely determined.

198. Tin and Titanium.—Tin contents as low as 0.29 per cent decreased the corrosion in 20 per cent H_2SO_4 and in the atmosphere, of Burgess and Aston's electrolytic iron.[274]

Increasing titanium from 0.1 to 0.9 per cent slightly increased solution of Swedish steel in 5 per cent HCl, HNO_3, and H_2SO_4 according to Endo,[775] as shown in Fig. 73.

199. Tungsten.—Small amounts of tungsten, 1 per cent or less, decreased the corrosion of electrolytic iron in 20 per cent H_2SO_4 and in the atmosphere, according to Burgess and Aston;[274] decreased corrosion in 10 per cent HCl, 10 per cent HNO_3, 10 per cent H_2SO_4, and in air at 1100°C.;[638] and decreased the rate of solution of Endo's Swedish steel in 5 per cent HCl, 5 per

cent HNO_3, and 5 per cent H_2SO_4.[775] Aitchison's results[323] indicated that 2 per cent tungsten was without appreciable effect on corrosion in sea water and tap water, and Friend[508] concluded that 0.4 per cent tungsten did not affect the corrodibility of a nickel-chromium steel. The effect of tungsten on the corrosion resistance of steels is discussed in more detail in a companion monograph in this series.[1054]
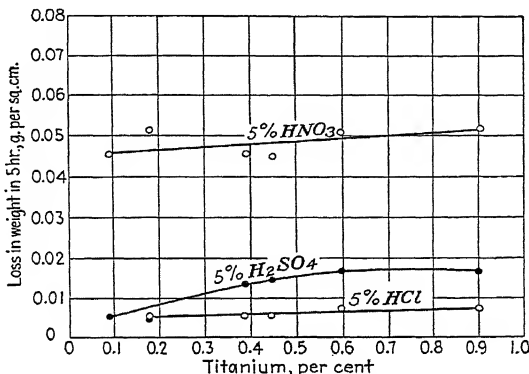
Fig. 73.—Effect of titanium on corrosion of Swedish iron in acids. (*Endo.*[775])

Small amounts of tungsten, if they affect the corrosion rate at all, tend to increase the resistance to corrosion.

200. Vanadium.—The presence of 0.7 per cent vanadium had no effect on the corrosion of iron immersed in tap water, 3 per cent NaCl solution, or sea water.[323,686] In acid solutions vanadium appeared to exert a detrimental effect, 1 per cent increased corrodibility in 5 per cent HNO_3 and considerably increased the attack of 5 per cent HCl and 5 per cent H_2SO_4 on Endo's Swedish steel.[775] The presence of 0.7 per cent or more did not exert an appreciable effect on corrosion in 1 per cent H_2SO_4 but was detrimental in 10 per cent H_2SO_4.[323] Corrosion was apparently accentuated by increasing vanadium.[576] Vanadium in amounts up to 5.4 per cent formed carbides, and increased corrosion.[659]

At best, vanadium is neutral in its effect on the corrosion of iron. It does not improve the resistance of iron to corrosion and in at least some cases it increases the corrodibility.

201. Summary of Effect of Impurities.—Generalities regarding the effect of impurities or added elements on the corrosion of iron are unsatisfactory. Evans[659] believed that added elements, such as chromium, nickel, or cobalt, which mainly entered into solid solution in the iron, tended on the whole to reduce corrosion in dilute sulphuric acid and sodium chloride solutions, but that elements such as vanadium, molybdenum, and tungsten, which mainly entered the carbide phase, did not appreciably reduce corrosion. In contrast to this view, Aitchison[323] concluded that the first additions of carbon, tungsten, chromium, cobalt, vanadium, nickel, or copper generally increased corrosion in tap water, in dilute sulphuric acid, or in sodium chloride solutions. Tiemann[1032] concluded that appreciable protection to iron was achieved only by the presence in solid solution of a considerable quantity of another element.

The divergence of opinion among different investigators in regard to the effect of small amounts of specific impurities apparently means that the effect of these impurities is less than the notoriously poor reproducibility of corrosion experiments. The effect of approximately 0.2 per cent copper on the corrosion of iron in the atmosphere is the one outstanding case of a beneficial effect from a small amount of added element and even in this case, the improvement is not due to an increased resistance to initial attack. Copper-bearing irons and steels rust rather rapidly at first during exposure to the atmosphere, but the type of rust coating which is produced serves to retard or to prevent further rusting, whereas in copper-free material subsequent attack is not retarded and may even be accelerated by the presence of rust.

F. AUTHORS' SUMMARY

Iron is not inherently resistant to corrosion. A fundamental cause for the corrosion of iron in the presence of water is that the solution pressure of iron is greater than that of hydrogen, which means that iron tends to dissolve in aqueous solutions with displacement of hydrogen ions. The extent of this tendency is indicated by the single potential of iron which is -0.44 volt with reference to the normal hydrogen electrode. The one inherent quality in iron, which promotes corrosion resistance, is the tendency to form passive films which protect the surface from

further attack. This tendency is particularly evident in very pure irons, but even in this case passivity cannot be depended upon for permanent protection against corrosion.

The effect of purity, in comparison of very pure irons with commercial products or in comparison of different grades of commercial products one with another, usually is less important than the effect of external conditions. Real resistance to corrosion is obtained only by the incorporation of considerable amounts of added elements, such as silicon in cast irons, or chromium and nickel in stainless steels, but even these products are not universally resistant to corrosion. The corrosion resistance of iron may be summarized in two words—iron rusts.

CHAPTER X

MECHANICAL PROPERTIES

Tensile Properties—Elastic Properties—Strength in Compression—Hardness—Resistance to Impact—Resistance to Fatigue—Properties at High and Low Temperatures—Plastic Deformation—Authors' Summary

This review of the literature on the mechanical properties of high-purity iron includes data on three types of material: (1) electrolytic iron, (2) commercial ingot iron, and (3) single-crystal specimens of high-purity iron. In some instances enough information is available on electrolytic iron to give a sufficiently complete view of the properties under consideration. In other instances it is necessary to substitute for, or to supplement, these data with experimental results obtained on commercially pure ingot iron. It is not the purpose of this review, however, to discuss exhaustively the mechanical properties of open-hearth ingot iron.

The properties of single crystals of iron are so obviously the fundamental properties of polycrystalline aggregates of iron and its alloys that they deserve detailed consideration whenever such information is available.

A. TENSILE PROPERTIES

In the ensuing discussion of tensile properties of iron definitions which have been used in preceding monographs of this series have been adopted. The property reported in the literature as elastic limit, proportional limit, or yield point has been designated yield strength if it was considered to represent the stress at which the material exhibited a specified limiting permanent set. Where possible the original term as used by the investigator has been given in a footnote. Most of the values for yield strength which are designated by a footnote below the table as yield point were determined by "drop-of-beam." Desch* stated

* Preprint, Manchester (England) meeting of Institution of Automobile Engineers and eleven other societies, March, 1935.

that soft iron and such steels as consist mainly of ferrite exhibit a pronounced yield point, as determined by the drop-of-beam method, but that this behavior does not appear to be characteristic of iron of the highest purity. In this respect very pure iron is comparable to other pure metals, copper for example, rather than to soft iron or to ferritic steels in the soft conditions.

202. Vacuum-fused Electrolytic Iron.—The tensile properties of electrolytic iron fused in vacuum were determined by Yensen, in connection with his studies of the magnetic properties of high-purity iron[321] and alloys of iron with silicon[342] and with aluminum.[386] Yensen's mechanical tests were made on 0.5-in.-diameter bars prepared from forged rods of the vacuum-fused iron. Tensile tests were made on the material as forged, after annealing treatments, and after quenching in brine and in liquid air. Yensen's doubly refined electrolytic iron, before melting in vacuum, contained 0.006 per cent carbon and 0.01 per cent silicon. The fused metal generally contained from 0.01 to 0.02 per cent carbon. Yensen found (Table 65) that the tensile

TABLE 65.—TENSILE PROPERTIES OF VACUUM-FUSED ELECTROLYTIC IRON*

No.	Known impurities, per cent		As forged				Quenched in brine from 1000°C. (1830°F.)			
	Carbon	Other impurities	Tensile strength, lb. per sq. in.	Yield strength,† lb. per sq. in.	Elongation in 1.5 in., per cent	Reduction of area, per cent	Tensile strength, lb. per sq. in.	Yield strength,† lb. per sq. in.	Elongation in 1.5 in., per cent	Reduction of area, per cent
1	....	....	68,000	64,000	22	81.5	40,500	....	53	84.5
2	......	......	......	......	..	....	44,900	....	44	86.0
3	....	....					35,400‡	15,500‡	45‡	36.6‡
4	0.008	....	55,500	51,400	32	85.8				
5	0.008	....					40,000	30,200	47	80.8
6	0.008	....	51,800	45,600	36	86.4				
7	0.009	....	44,800	36,600	41	87.7				
8	0.009	....	......	......	..	....	55,500	....	32	83.1
9	0.010	....	......	......			45,500	37,400	42	86.1
10	0.010	....	65,500	62,200	26	83.8				
11	0.010	....	......	38,200	35					
13	0.011	....	44,700	35,800	39	80.4				
14	0.011	....	43,500	39,600	38	82.3				
15	0.012	....	70,500	69,100	20	82.8				
16	0.012	....	48,700	41,400	44	76.2				
17	0.012§	....	......	......	..	....	76,900	67,700	25	79.7
18	0.013‖	....					53,000	33,200	65	86.2
19	<0.015	....	54,700	50,700	26	84.3				
20	<0.015	0.02Al¶	46,400	40,200	28	93.4				
23	0.045	....	......	......	..	....	64,600	41,250	37	73.7

* Yensen.[321,386]
† Reported as yield point.
‡ Quenched in liquid air.
§ Carbon equivalent to 0.10 per cent added to melt.
‖ Carbon equivalent to 0.05 per cent added to melt.
¶ Aluminum equivalent to 0.1 per cent added to melt.

TABLE 65.—TENSILE PROPERTIES OF VACUUM-FUSED ELECTROLYTIC IRON.*—(Continued)

No.	Known impurities, per cent		Annealed at 900°C. (1650°F.), cooled in 12 hr.				Annealed at 900°C. (1650°F.), cooled in 24 hr.			
	Carbon	Other impurities	Tensile strength, lb. per sq. in.	Yield strength,† lb. per sq. in.	Elongation in 1.5 in., per cent	Reduction of area, per cent	Tensile strength, lb. per sq. in.	Yield strength,† lb. per sq. in.	Elongation in 1.5 in., per cent	Reduction of area, per cent
2	....	....	......	......	..	....	34,500	14,400	54	87.3
4	0.008	....	39,400	15,000	40	88.0				
5	0.008	....	36,100	17,400	57	91.3				
6	0.008	....	......	......	..	....	35,800	15,300	42	73.2
8	0.009	....	......	......	..	....	34,300	....	47	61.1
9	0.010	....	......	......	..	....	35,150	....	56	85.5
10	0.010	....	40,200	......	53	85.1				
11	0.010	....	......	......	..	....	35,800	19,300	45	86.5
12	0.010	....	35,800	18,750	59	84.5				
13	0.011	....	......	......	..	....	36,100††	16,400††	61††	80.9††
14	0.011	....	41,600	......	42	85.7				
15	0.012	....	35,500	20,700	60	89.5				
16	0.012	....	......	......	..	....	34,900	11,100	32	75.7
17	0.012§	....	38,900	19,400	60	73.5				
18	0.013‖	....	51,100	21,000	41	72.5				
19	<0.015	....	......	......	..	....	34,900§§	17,600§§	60§§	93.5§§
20	<0.015	0.02Al¶	......	......	..	....	34,450§§	13,900§§	60§§	91.6§§
21	<0.015	Tr. Al**	......	......	..	....	32,100§§	14,000§§	48§§	65.7§§
22	0.015	....	......	......	..	....	37,500	20,100	52	77.0

* Yensen.[321,386]
† Reported as yield point.
§ Carbon equivalent to 0.10 per cent added to melt.
‖ Carbon equivalent to 0.05 per cent added to melt.
¶ Aluminum equivalent to 0.1 per cent added to melt.
** Aluminum equivalent to 0.4 per cent added to melt.
†† Cooled in 48 hr.
§§ Annealed at 1000°C. (1830°F.), cooled in 33 hr.

strength of annealed iron was approximately 35,000 to 40,000 lb. per sq. in. and the yield strength was 10,000 to 20,000 lb. per sq. in. The elongation was 40 to 60 per cent (in a 1.5-in. gage length); the reduction of area was between 70 and 90 per cent. The iron as forged had tensile strengths of the order of 45,000 to 65,000 lb. per sq. in. Specimens quenched from 1000°C. (1830°F.) into brine had tensile strengths of 45,000 to 50,000 lb. per sq. in.

Mechanical properties of vacuum-melted electrolytic iron were also reported by Neville and Cain.[481] Their tensile tests were made on bars which had been heated at 940°C. (1725°F.) and then cooled in still air. The iron contained 0.02 per cent carbon, 0.011 per cent sulphur, 0.004 per cent silicon, and no manganese. The tensile strengths of two specimens were 41,700 and 42,200 lb. per sq. in., the elongations in 2 in. were 40 and 41 per cent, and the reductions of area, 80 and 85 per cent.

Electrolytic iron (0.01 per cent carbon, 0.009 per cent phosphorus, 0.008 per cent sulphur, and traces of silicon and manganese) which had been vacuum fused and annealed at 700°C. (1290°F.) was found by Körber and Rohland[568] to have a tensile strength of 32,400 lb. per sq. in., an elongation of 44 per cent (in a gage length five times the diameter of the specimen), and a reduction of area of 83 per cent.

Tritton and Hanson[585] prepared electrolytic iron specimens with the primary object of studying the effect of oxygen. One of their fused alloys contained 0.08 per cent oxygen, 0.007 per cent phosphorus, and traces of carbon, silicon, sulphur, and manganese. This material had a tensile strength of 34,100 lb. per sq. in., a yield strength of 18,600 lb. per sq. in., an elongation of 50 per cent (in a gage length four times the square root of the cross-sectional area), and a reduction in area of 80 per cent.

Vacuum-fused electrolytic iron, prepared by Heraeus and containing 0.02 per cent carbon, 0.01 per cent manganese, 0.02 per cent silicon, 0.006 per cent sulphur, 0.01 per cent phosphorus, and a trace of copper, was reported by Körber and Hoff[792] to have, in the annealed condition, a tensile strength of 34,100 lb. per sq. in. and an elongation of 29.5 per cent in 2 in. (5 cm.).

203. Electrodeposited Iron (Not Fused).—In several instances tensile properties have been determined on specimens of electrolytic iron either as deposited or after simple annealing treatment.

Such tests of electrolytic iron made at Grenoble, France, were reported by Escard.[397] This iron annealed at 900°C. (1650°F.) had a tensile strength of 44,000 to 46,600 lb. per sq. in. and an elongation of 40.3 to 43.1 per cent (gage length not given). Bouchayer[499] reported tensile properties for Grenoble electrolytic iron both as deposited and after annealing at 950°C. (1740°F.). The iron as deposited had a tensile strength of 113,500 lb. per sq. in., a yield strength of 111,000 lb. per sq. in., and an elongation of only 3 per cent. After annealing, its tensile strength was 42,300 lb. per sq. in., yield strength 25,200 lb. per sq. in., and elongation 43 per cent.

Hutchins[567] annealed electrolytic iron tubes at 1000°C. (1830°F.), cut the tubes longitudinally and opened them up to form sheets, then cut test specimens which were finally annealed at 960°C. (1760°F.). The iron contained 0.031 per cent carbon, 0.02 per cent manganese, traces of silicon, sulphur, and phos-

phorus, and no copper or nickel. The tensile strength of the annealed iron was 41,900 lb. per sq. in., the yield strength from 19,000 to 20,400 lb. per sq. in., and the elongation (in 1 in.) from 26 to 39 per cent.

Additional tests on Grenoble iron, reported[757] as made by the National Tube Company on electrolytic iron tubes, gave a tensile strength of 61,800 lb. per sq. in. with an elongation of 12 per cent in 8 in. for the material as received, and a tensile strength of 39,000 lb. per sq. in. with an elongation of 30 per cent after annealing at 900°C. (1650°F.) for 20 min.

Some of the mechanical properties of the electrolytic iron as deposited in the production of intaglio printing plates at the Bureau of Engraving and Printing in Washington, D. C., were reported by Thomas and Blum[911] and are shown in Table 66. The samples, which have no annealing treatment indicated, were tested "as deposited" from a ferrous chloride–calcium chloride bath operated at 90°C. (195°F.).

TABLE 66.—TENSILE PROPERTIES OF ELECTRODEPOSITED IRON,* NOT FUSED†

Method of agitation of electrolyte	Temperature of 1-hr. anneal		Tensile strength, lb. per sq. in.	Elongation in 2 in., per cent
	°C.	°F.		
Air.....................	...	...	55,500	5.6
Mechanical..............	...	...	55,600	20.0
Mechanical..............	100	210	56,100	19.0
Mechanical..............	200	390	55,300	25.0
Mechanical..............	300	570	55,900	27.0

* Chemical composition of iron after fusion in MgO refractory in vacuum furnace: 0.013 per cent carbon, 0.005 per cent sulphur, 0.003 per cent silicon, 0.02 per cent copper, 0.01 per cent nickel, manganese and phosphorus not detected.
† Thomas and Blum.[911]

The data of Table 66 indicate no change in the tensile strength or elongation of the iron "as deposited," as a result of annealing at 100, 200, or 300°C. (210, 390, or 570°F.). Agitation of the electrolytic bath by air very noticeably decreased the elongation but did not affect the tensile strength as compared with the iron produced with mechanical agitation. Thomas and Blum stated that samples from air-agitated baths had elongations ranging

from 0 to 12 per cent. The ductility of the iron deposited with mechanical agitation was indicated by the fact that it was possible to bend plates as deposited (with a thickness of about 0.2 in.) around cylinders less than 8 in. in diameter provided that the face of the plate (the surface first deposited) was on the convex side. A plate bent in the opposite direction was brittle, evidently due to the coarse conical crystals in the last portions of the metal to deposit, as compared with the fine-grained metal in the initially deposited layers.

Pike[901] reported the tensile strength of electrolytic iron (0.005 per cent carbon, 0.007 per cent sulphur, 0.006 per cent copper) deposited as a plate somewhat more than 0.2 in. thick, machined to 0.2 in. in order to produce a smooth surface, then cold rolled to 0.109 in., and finally annealed. The tensile strength was 35,300 lb. per sq. in. and the elongation was 14 per cent in 2 in. The test was made in the direction parallel to the direction of rolling.

204. Open-hearth Ingot Iron.—The data in Table 67 enable a comparison to be made of the tensile properties of several electrolytic irons with those of commercially pure irons such as Armco open-hearth ingot iron or Krupp's special soft iron. Typical analysis of Armco iron shows that 0.013 per cent carbon, 0.017 per cent manganese, 0.005 per cent phosphorus, 0.025 per cent sulphur, 0.04 per cent copper, and traces of silicon are present. The data for Armco iron in Table 67 were obtained by Kenyon[787] from rods of hot-rolled material. The data for Krupp's special soft iron were reported by Goerens and Fischer.[413] Analyses of five heats showed that the metal contained, on an average, 0.057 per cent carbon, 0.097 per cent manganese, 0.021 per cent sulphur, and less than 0.01 per cent each of silicon and phosphorus.

205. Other High-purity Irons.—The "hydrogenized" iron prepared by Cioffi[964] by treating ingot iron in hydrogen at temperatures of 1475 to 1500°C. (2685 to 2730°F.) was reported to have a tensile strength of only 14,000 lb. per sq. in. and a yield strength of 7000 lb. per sq. in. Although it was not indicated that the particular specimens which were used in the tensile tests were of large grain size, it was stated that very coarse grains are characteristic of this material. These values for the tensile properties of "hydrogenized" iron are, therefore, included and

Table 67.—Summary of Tensile Properties of Various Electrolytic Irons and of Commercial Open-hearth Iron

Condition of material	Tensile strength, lb. per sq. in.	Yield* strength, lb. per sq. in.	Elongation		Reduction of area, per cent	Investigator
			Per cent	Gage length, in.		
Vacuum-fused electrolytic iron						
Annealed...............	35,000 to 40,000	10,000 to 20,000	40 to 60	1.5	70 to 90	Yensen[321,386]
Forged.................	45,000 to 65,000	40,000 to 65,000	25 to 40	1.5	75 to 85	Yensen[321,386]
Quenched in brine.......	45,000 to 65,000	15,000 to 40,000	30 to 60	1.5	75 to 85	Yensen[321,386]
Annealed...............	42,000	....	40	2.0	80 to 85	Neville and Cain[481]
Annealed...............	32,400	....	44	$5 \times$ diam.	83	Körber and Rohland[568]
Annealed...............	34,100	18,600	50	$4\sqrt{A}$	80	Tritton and Hanson[585]
Annealed...............	34,100	....	29.5	2.0	..	Körber and Hoff[792]
Electrolytic iron not fused						
Annealed (Grenoble iron)	44,000 to 47,000		42			Escard[397]
As deposited (Grenoble iron).................	113,500	111,000	3	†		Bouchayer[499]
Annealed (Grenoble iron)	42,300	25,200	43	†		Bouchayer[499]
Annealed...............	41,900	19,500	26 to 39	1.0		Hutchins[567]
Tubes, as received, (Grenoble iron).......	61,800		12	8.0		Anonymous [757]
Tubes, annealed, (Grenoble iron).......	39,000		30	8.0		Anonymous [757]
Printing plates; as deposited.............	55,600		20	2.0		Thomas and Blum[911]
Same; annealed up to 300°C. (570°F.).......	55,300 to 56,100		19 to 27	2.0		Thomas and Blum[911]
Plate, cold rolled, annealed...............	35,300		14	2.0		Pike[901]
Open-hearth ingot iron						
Hot-rolled rods (Armco).	42,000 to 45,000	26,000 to 37,000	25 to 38	8.0	70 to 76	Kenyon[787]
Rolled or forged bars, annealed (Krupp's)......	43,100 to 45,500	29,900 to 32,700	35 to 38	$10 \times$ diam.	79 to 80	Goerens and Fischer[413]
Sheets, annealed (Krupp's)............	43,700 to 45,500	28,400 to 31,300	32 to 33	†	77 to 78	Goerens and Fischer[413]

* Reported as "yield point" in most cases.
† Not given.

compared with the data of the next section on tests of single-crystal and very coarsely crystalline specimens.

Iron prepared by sintering and hammering carbonyl-iron powder was reported by Duftschmid, Schlecht, and Schubardt[965] to have a tensile strength of 28,000 to 40,000 lb. per sq. in., a yield strength of 15,500 to 24,000 lb. per sq. in., an elongation of 30 to 40 per cent, and a reduction of area of 70 to 80 per cent.

206. Single Crystals of Iron.—Among the earliest, if not the first, measurements of mechanical properties of single crystals of relatively pure iron are those reported by Osmond and Frémont.[134] They prepared test specimens from large iron crystals which had developed spontaneously in a steel rail in service as a furnace brace for some 15 years. No detailed information was given as to the purity of the iron except the statement that it had been decarburized, and that other impurities had been removed by oxidation, leaving a rather pure iron. Osmond and Cartaud,[148] however, gave the following for the composition of what is apparently the material originally reported by Osmond and Frémont: 0.06 per cent carbon, 0.05 per cent silicon, 0.30 per cent manganese, 0.02 per cent sulphur, and 0.116 per cent phosphorus.

A single tensile specimen was prepared with its axis parallel to an axis of the cubic crystal of iron, *i.e.*, with the axis of the test bar perpendicular to a cube face. This specimen had a tensile strength of 39,500 lb. per sq. in., a yield strength of 23,500 lb. per sq. in., and a reduction of area of 85 per cent. Osmond and Frémont also determined the elastic limit of a test specimen which had a cylindrical section 8 mm. (0.3 in.) in diameter and 10 mm. (0.39 in.) long. The ends of the specimen were truncated cones 28 mm. (1.1 in.) long with the larger base 16 mm. (0.6 in.), and the smaller base 8 mm. (0.3 in.) in diameter, *i.e.*, the diameter of the reduced section. After the specimen had been broken in tension, the point to which the polish had been destroyed on the conical surfaces was observed and the stress attained at that point was calculated to be between 18,500 and 22,800 lb. per sq. in. This value was termed the elastic limit.

Edwards and Pfeil[553] decarburized in moist hydrogen mild steels which originally contained approximately 0.1 per cent carbon, 0.02 per cent silicon, 0.04 per cent manganese, 0.03 to

0.05 per cent sulphur, and 0.02 per cent phosphorus. Specimens of the decarburized iron (possibly also somewhat purified as regards sulphur) were strained and annealed to produce large crystals, and test bars were cut from large crystal sections so that the parallel portion of the test bars (2.5 in. × 0.75 in. × 0.125 in.) was in each case a single crystal. The tensile strength and the elongation (in 2 in.) were determined on the original mild steel, the decarburized, but still fine-grained material, and on the decarburized, single-crystal test bars. These values compared as follows:

Property	Original steel	Decarburized, fine grain	Decarburized, single crystal
Tensile strength, lb. per sq. in...	72,600	43,900	20,000 to 22,400
Elongation in 2 in., per cent....	22	53.5	30 to 50

Additional tests on 10 large single-crystal specimens[603] gave, in all except two tests, tensile strengths of approximately 22,400 lb. per sq. in., thus agreeing with the tensile strength of single crystals of iron found in Edwards and Pfeil's original tests on four specimens. One specimen of this second series

TABLE 68.—TENSILE PROPERTIES OF LARGE SINGLE CRYSTALS OF IRON*

Specimen No.	Tensile strength, lb. per sq. in.	Yield strength,† lb. per sq. in.	Elongation in 2 in., per cent	Modulus of elasticity, million lb. per sq. in.
1	21,000	4300	33.5	29.8
2	21,400	5500	31.0	27.4
3	21,400	5600	35.0	27.0
4	21,700	5100	35.8	25.1
5	22,600	3900	32.3	27.2
6	23,100	4500	30.5	28.1
7	23,600	4800	41.5	28.8
8	23,900	5100	52.5	26.6
9	25,500	4700	44.5	22.4
10	34,500	4400	53.7	26.7

* Edwards and Pfeil.[603]
† Reported as proportional limit.

had a tensile strength of 34,500 lb. per sq. in. Values for yield strength (reported as proportional limit), elongation, and modulus of elasticity were also determined on these iron single crystals (Table 68). The exact orientations were not determined but it was known that the orientations of the 12 crystals that had tensile strength of about 22,000 lb. per sq. in. were not identical.

Another series of similar tests was made by Edwards and Pfeil on smaller single crystals—crystals of a size permitting only 1.5-in. parallel portions in the test bars and 1-in. gage lengths. These specimens gave more variable results for tensile strength (Table 69) than did the larger crystal specimens. Seven

TABLE 69.—TENSILE PROPERTIES OF SMALL SINGLE CRYSTALS OF IRON*

Specimen No.	Tensile strength, lb. per sq. in.	Elongation in 1 in., per cent
30	21,700	55.5
31	21,800	66.0
32	22,200	60.0
33	22,300	33.5
34	22,300	50.0
35	22,300	53.0
36	22,400	52.5
37	27,600	72.0
38	30,700	66.0
39	31,400	84.5
40	33,200	58.0

* Edwards and Pfeil.[503]

of eleven tests again gave approximately 22,000 lb. per sq. in., but the other four tests gave results varying from 27,000 to 33,500 lb. per sq. in.

207. Effect of Crystal Size.—Following this consideration of the effect of the size of single crystals upon the tensile strength of iron, Edwards and Pfeil prepared two series of specimens, one from material identical with that used in the previous tests, the second from material of slightly different composition but treated like the first series, in order to study the effect of progressively finer grain size upon the mechanical properties, that is, to bridge the gap between single-crystal specimens and ordinary poly-

crystalline material. Specimens were prepared with crystal sizes ranging from coarse crystals of average diameters of 9.7 mm. to fine crystals of such sizes that about 300 occupy 1 sq. mm.

TABLE 70.—EFFECT OF GRAIN SIZE ON TENSILE PROPERTIES OF IRON*

Specimen No.	Grain size, grains per sq. mm.	Tensile strength, lb. per sq. in.	Yield strength,† lb. per sq. in.	Elongation in 2 in., per cent
		Series 1		
1	9.7‡	23,900	5,900	28.8
2	7.0‡	26,200	5,600	30.5
3	2.5‡	30,600	6,400	39.5
4	6.3	33,700	6,500	35.3
5	15.3	36,600	6,200	47.0
6	35.6	38,200	8,300	48.8
7	48.8	38,300	9,400	50.7
8	51.0	38,900	10,000	44.8
9	75.5	42,000	20,100	47.0
10	77.5	41,600	20,200	48.3
11	91.6	40,000	16,600	50.3
12	92.0	40,300	16,800	50.0
13	120	41,200	16,700	42.5
14	130	41,600	15,700	41.3
15	194	41,900	15,400	47.5
		Series 2		
1	27	38,500	8,400	41.3
2	34	39,300	10,500	41.3
3	53	38,600	7,700	46.3
4	57	38,000	10,700	38.8
5	78	38,500	11,300	33.5
6	84	39,600	12,100	51.3
7	98	42,300	14,700	46.0
8	98	43,100	15,500	46.5
9	102	42,600	16,300	44.8
10	108	44,400	15,800	46.3
11	109	42,800	15,100	42.8
12	113	42,200	14,500	47.8
13	118	43,100	18,000	48.5
14	127	43,200	19,500	44.0
15	135	43,300	22,200	45.3
16	157	44,200	22,600	45.3
17	168	38,100	15,700	45.0
18	203	38,200	14,200	44.8
19	230	37,700	13,800	48.0
20	245	37,300	14,000	45.5
21	307	39,100	13,800	48.3

* Edwards and Pfeil.[603]
† Reported as proportional limit.
‡ Diameter of average crystal in mm.

The latter size represented the mild steel simply decarburized but not treated to produce grain growth. Edwards and Pfeil's data on the effect of grain size are given in Table 70. In the discussion of their paper the maxima indicated in yield strength and tensile strength at specimen 10 of series 1 and specimens 15 and 16 of series 2 were criticized as not necessarily due to grain size but possibly related to differences in the treatments which were necessary to produce the different grain sizes.

Ziegler[913] reported a tensile test of a single crystal of open-hearth ingot iron, which had the following properties:

Tensile strength...................... 22,100 lb. per sq. in.
Yield strength....................... 9,300 lb. per sq. in.
Elongation (2 in.)................... 55.5 per cent

He prepared a series of specimens of this same iron and studied the effect of grain size on tensile strength and yield strength. His results can be compared with those of Edwards and Pfeil only within a relatively short range of the larger grain sizes since Ziegler's smallest grains were of the order of 40 per sq. mm. Within this range of grain size the tensile strength increased gradually from 22,100 lb. per sq. in. to 35,800 lb. per sq. in. and the yield strength (yield point) from 9300 lb. per sq. in. to 16,300 lb. per sq. in.

208. Summary of Data on Tensile Properties.—Available information indicates that electrolytic iron in the as-deposited condition may have tensile strengths and yield strengths of more than 100,000 lb. per sq. in. with elongations as small as 3 per cent. However, the properties of the same material in the annealed condition are roughly comparable to those of Armco iron. The tensile strength of annealed electrolytic iron is reported to be between 40,000 and 55,000 lb. per sq. in., yield strength between 20,000 and 25,000 lb. per sq. in., with elongations between 25 and 45 per cent. Fusion in vacuum with subsequent annealing treatment further softens electrolytic iron. The reported properties of such material are: tensile strength between 35,000 and 40,000 lb. per sq. in., yield strength between 10,000 and 20,000 lb. per sq. in., elongation between 30 and 60 per cent, and reduction of area between 70 and 90 per cent.

Data for the tensile properties of single crystals are available only for material which approximates the composition of Armco

iron. For such material an increase in grain size does not appreciably affect the tensile properties until the grains reach a size of approximately 25 per sq. mm. For larger grains an increase in size is accompanied by softening; the properties of single crystals (presumably with low carbon contents) have been reported as tensile strengths of 20,000 to 35,000 lb. per sq. in., yield strengths of 4000 to 9000 lb. per sq. in., and elongations of 30 to 85 per cent.

B. ELASTIC PROPERTIES

Values for Young's modulus, for different directions in a single crystal of Armco iron, were determined by Goens and Schmid.[967] They found that Young's modulus was more than twice as great in the direction of the cube diagonal (the [1 1 1] direction) as in the direction of the cube axis (the [1 0 0] direction). The values found for Young's modulus were as follows:

$E_{[1\ 0\ 0]}$ = 19,000,000 lb. per sq. in. (13,500 kg. per sq. mm.)
$E_{[1\ 1\ 1]}$ = 41,000,000 lb. per sq. in. (29,000 kg. per sq. mm.)

In a recent report from the National Physical Laboratory, Abram[1041] found that Armco iron and mild steel have a definitely greater modulus of elasticity than medium- and high-carbon steels. From these results Abram deduced that Young's modulus of pure iron in the annealed condition would be about 30,000,-000 lb. per sq. in., a value which is intermediate between the two values obtained by Goens and Schmid for different directions in a single crystal.

From determinations of Young's modulus and the modulus of torsion of single-crystal specimens of iron, Kimura and Ohno[1059] computed the elastic moduli in the direction of the principal crystallographic axes, as follows:

$$\begin{array}{l}
\text{Young's modulus,} \\
\text{dynes per} \\
\text{sq. cm.}
\end{array}
\left.\begin{array}{l}
E_{[1\ 0\ 0]} = 1.30_7 \times 10^{12} \\
E_{[1\ 1\ 0]} = 2.16_4 \times 10^{12} \\
E_{[1\ 1\ 1]} = 2.77_1 \times 10^{12}
\end{array}\right.$$

$$\begin{array}{l}
\text{Modulus of} \\
\text{torsion,} \\
\text{dynes per} \\
\text{sq. cm.}
\end{array}
\left\{\begin{array}{l}
n_{[1\ 0\ 0]} = 1.11_7 \times 10^{12} \\
n_{[1\ 1\ 0]} = 0.66_0 \times 10^{12} \\
n_{[1\ 1\ 1]} = 0.58_7 \times 10^{12}
\end{array}\right.$$

From these values the fundamental constants (Voight's modulus) and the elastic constants were computed, as follows:

Voight's modulus, dynes per sq. cm.

$= (0.765_2 \pm 0.005_3) \times 10^{-12}$
$= -(0.288_8 \pm 0.008_2) \times 10^{-12}$
$= (0.895_2 \pm 0.010_9) \times 10^{-12}$

Elastic constants, dynes per sq. cm.

$= 2.40_9 \times 10^{12}$
$= 1.46_1 \times 10^{12}$
$= 1.11_7 \times 10^{12}$

C. STRENGTH IN COMPRESSION

Little attention appears to have been paid to compression tests of very pure iron except in such work as has been done with single crystals. There are, of course, data on compression tests of commercially pure iron.

209. Open-hearth Ingot Iron.—Kenyon[787] gave values, originally reported by Moore and Kommers,[443] as typical of open-hearth iron (Armco iron) in compression tests. The tests were made on material from normalized hot-rolled 1-in. round bars. Elastic limit (as indicated by first permanent set after release of load), proportional limit (stress at which stress-strain curve had a slope 25 per cent greater than its initial slope), and yield strength (reported as yield point) were as follows:

Elastic limit...................... 19,400 lb. per sq. in.
Proportional limit.................. 19,200 lb. per sq. in.
Yield strength..................... 20,600 lb. per sq. in.

210. Single Crystals.—Osmond and Frémont[134] made compression tests on single-crystal specimens from the material already described in the discussion of the tension tests. They determined values for yield strength in compression, making the measurements on two specimens, one compressed with the loading normal to a cube face, the other with the loading normal to an octahedral face. The iron had previously been annealed at about 800°C. (1470°F.). The following results were obtained for yield strength:

Compression on cube faces............ 19,800 lb. per sq. in.
Compression on octahedral faces...... 24,200 lb. per sq. in.

Following the work by Edwards and Pfeil[553,603] on the tensile properties of single crystals and on the influence of grain size on the tensile properties of iron, Pfeil[681] continued the work with single crystals and prepared specimens for compression tests. The steel employed for the production of the single crystals was

in the form of 0.5-in. diameter rods and contained 0.10 per cent carbon, 0.064 per cent silicon, 0.46 per cent manganese, 0.034 per cent sulphur, 0.02 per cent phosphorus.   This steel was completely decarburized by heating in hydrogen for 2 to 3 weeks and was then treated to produce single crystals of 0.5 in. diameter and, as a rule, from 1.5 to 3 in. long.   Compression specimens 0.45 in. in diameter and 0.9 in. long were cut from single crystals. The orientation of the crystal lattice within the test specimen was determined by means of the patterns produced by needle-point indentations made in discs cut from the same crystal.   Compression tests were made on specimens of several crystal orientations.   The stress at which slip lines were first observed upon the cylindrical surface of the specimen was recorded, as well as the stress which produced a permanent deformation of 0.01 per cent (the "measured elastic limit").   These values, as well as the compressive stresses which produced permanent deformations of 0.1, 1.0, and 10 per cent, are given in Table 71.   Pfeil concluded that "the iron crystal has the highest elastic limit when compressed on a rhombododecahedral plane and the lowest when compressed on a cube plane."

211. Summary of Data for Strength in Compression.—Data for compression tests of high-purity iron are not available. For polycrystalline Armco iron the elastic limit and proportional limit in compression are about 19,000 lb. per sq. in.; the yield strength is about 20,000 lb. per sq. in.   The limited data which are available indicate that the resistance of single crystals to compression varies with the orientation and is at a minimum when the crystal is compressed on a cube face.

D. HARDNESS

In the ensuing discussion the hardness data have been divided into groups according to the nature and previous history of the material.

212. Cathode Electrolytic Iron.—Electrolytic iron as deposited is frequently much harder than the same material after annealing or after fusion.   There is much discussion in the literature as to whether this initial hardness is caused by the presence of hydrogen in the electrodeposited iron or is to be attributed to the small grain size of the iron.

TABLE 71.—COMPRESSION PROPERTIES OF IRON SINGLE CRYSTALS*

Specimen	Orientation†	Stress at which slip lines appeared, lb. per sq. in.	Measured elastic limit,‡ lb. per sq. in.	Stress, in lb. per sq. in., for permanent deformation of			
				0.1 per cent	1.0 per cent	10 per cent	25 per cent
1	(1 1 0)	4800	6400	8300	11,300	27,700	51,000
2	(1 1 0)	4900	7100	9100	11,400	42,600	50,600
3	(1 1 0)		6500	8000	10,400	24,400	44,600
4	(1 1 0)	5200	6400	7500	(8,800)	(23,600)	(46,600)
Average		5000	6600	8200	11,000	28,300	48,800
5	Near (1 1 0)		6900	8200	10,800	27,300	52,600
6	Near (1 1 0)	4500	5700	7500	10,400	30,700	53,100
7	Near (1 1 0)	3600	5900	7700	10,500	30,200	55,300
8	Near (1 1 0)	....	6800	9000	12,600	30,700	
Average		4000	6300	8100	11,100	29,800	53,500
9	(1 1 0)–(1 1 1)	4900	6800	9400	14,100	33,400	49,700
10	(1 1 0)–(1 1 1)	4300	6300	7900	10,300	28,000	56,900
11	(1 1 0)–(1 1 1)	4900	6000	8800	13,200	35,800	59,100
12	(1 1 0)–(1 1 1)	5300	6300	8400	12,200	31,800	55,300
13	(1 1 0)–(1 1 1)	....	5700	7800	11,900	35,400	56,200
Average		4800	6200	8400	12,300	32,900	55,600
14	(1 1 1)		6200	8900	12,800		
15	(1 1 0)–(1 0 0)	5500	6700	8600	12,700	30,700	44,800
16	Near (1 0 0)	4100	4800	7700	11,800	33,400	44,100
17	Near (1 0 0)	4800	5700	8000	11,900	29,100	
Average		4400	5200	7900	11,800	31,200	
18	(1 0 0)	3700	5400	8900	13,400	32,500	45,000
19	(1 0 0)	4500	5800	9100	13,100	30,900	43,700
20	(1 0 0)	4700	5200	8000	14,100	36,500	46,100
Average		4200	5400	8600	13,500	33,400	45,000

* Pfeil.[681]

† The orientation is given approximately: (1 0 0) represents the compression on a cube face; (1 1 0) on a rhombohedral face; (1 1 1) on an octahedral face; (1 0 0)–(1 1 1) stands for compression on a face between that of a cube and that of an octahedron, etc.

‡ Stress giving first permanent deformation of 0.01 per cent.

Cathode iron as deposited has been reported by various investigators (Table 72) as having a Brinell hardness number from 180 to as high as 360; the Brinell of the same material after annealing is from 50 to 90. The Brinell hardness of electrolytic iron, freshly deposited and consequently saturated with hydrogen, was found by Guillet and Portevin[282] to be 140 (10 mm. ball, 3000 kg. load). This value decreased to 90 upon annealing the

iron for 2 hr. at 900°C. (1650°F.).   Guichard *et al.*[887] annealed electrolytic iron, of an initial Brinell of 360 (3 mm., 40 kg., 30 sec.), at various temperatures up to 1000°C. (1830°F.).   They found that all of the hydrogen obtainable from the iron by heating

TABLE 72.—BRINELL HARDNESS OF ELECTROLYTIC IRON

Condition of specimen	Conditions of test			Brinell hardness	Investigator
	Ball diameter, mm.	Load, kg.	Time, sec.		
Cathode iron					
As deposited.....	10	3000	..	140	Guillet and Portevin[282]
Annealed........	10	3000	..	90	Guillet and Portevin[282]
As deposited.....	3.18	125	..	179	Bouchayer[499]
Annealed........	3.18	125	..	76	Bouchayer[499]
As deposited.....	1	30	..	180–350	MacNaughton[570]
Annealed........	1	30	30	77	Hutchins[567]
As deposited.....	10	3000	..	193	Anonymous[757]
Annealed........	10	3000	..	90	Anonymous[757]
As deposited.....	3	40	30	360	Guichard *et al.*[887]
Annealed........	3	40	30	50	Guichard *et al.*[887]
Vacuum-fused iron					
Annealed........	5	197	60	58	Bauer and Schneider[429]
Normalized......	.....	....	..	70	Neville and Cain[481]
As melted.......	5	750	30	66	Tritton and Hanson[585]

had been removed by the time the iron had reached 240°C. (465°F.); there was no further evolution of gas during heating to a maximum temperature of 1000°C. (1830°F.).   However, the extreme hardness of the initial material did not decrease until the iron was heated above 240°C. (465°F.).   The hardness then decreased rather rapidly, reaching a Brinell of about 50 after annealing at 1000°C. (1830°F.).   These authors concluded that the extreme hardness of freshly deposited electrolytic iron was not to be attributed to its hydrogen content but rather to its small grain size.

An interesting observation, quite different from the results of others, was made by Pilling[485] in a study of the relation of

scleroscope hardness to the temperature of annealing of electro-deposited iron. Pilling found that electrolytic iron with an initial scleroscope hardness of about 26 maintained this after annealing at 100 and 200°C. (210 and 390°F.). Annealing at 300°C. (570°F.) produced a marked increase, to 45 scleroscope, and thereafter successively higher annealing temperatures progressively lowered the hardness. Hadfield later tried without success to induce increased hardness in electrolytic iron by similar treatments.[564]

A study of the influence of hydrogen-ion concentration, current density, and temperature of the electrolyte upon the hardness of electrolytic iron was made by MacNaughton.[570] He found the general effect of increasing the acidity of the electrolyte, within the range of pH 4.5 to pH 3.3, was to increase the Brinell number (1 mm., 30 kg.) from about 180 to about 270, the current density being 4.7 amp. per sq. ft. and the temperature of the electrolyte being about 20°C. (68°F.). Iron deposited from the electrolyte at room temperature and at a pH of 4.4 had Brinell numbers increasing from about 180 to 350 as the current density increased from 5 to 20 amp. per sq. ft. Iron deposited at a current density of 50 amp. per sq. ft. at 41°C. (105°F.) had a Brinell hardness of 240.

Hadfield in discussing MacNaughton's work recorded Brinell numbers of about 200 for electrolytic iron as deposited, the maintenance of this hardness after annealing up to 350°C. (660°F.), the lowering to about 160 by annealing at 500°C. (930°F.), and finally to 90 by annealing at 900°C. (1650°F.).

213. Fused and Compacted Iron.—Scratch-hardness values for unmelted, fused, and fused and quenched electrolytic iron were determined by Boynton.[139] His measurements, made with a microsclerometer, indicated that the unmelted iron was somewhat harder than the same material after fusion. Boynton's most interesting observation, however, was that quenching the fused electrolytic iron from 850°C. (1560°F.) or from 1300°C. (2370°F.) into carbon dioxide snow appreciably increased the hardness. Bauer and Schneider[429] later made similar quenching experiments and found that the Brinell hardness of electrolytic iron quenched from various temperatures between 650 and 1250°C. (1200 and 2280°F.) showed no tendency to change with increasing quenching temperatures. All of the Brinell numbers

(5 mm., 197 kg., 1 min.) which they reported lay between 55 and 59.

The Brinell hardness of vacuum-melted electrolytic iron apparently lies between 60 and 70 (Table 72).

Other forms of fused or compacted high-purity iron for which hardness data are available are the "hydrogenized" iron prepared by Cioffi[964] and the carbonyl iron tested by Koch and Seefeldner and reported by Duftschmid.[965]   Cioffi reported that hydro-
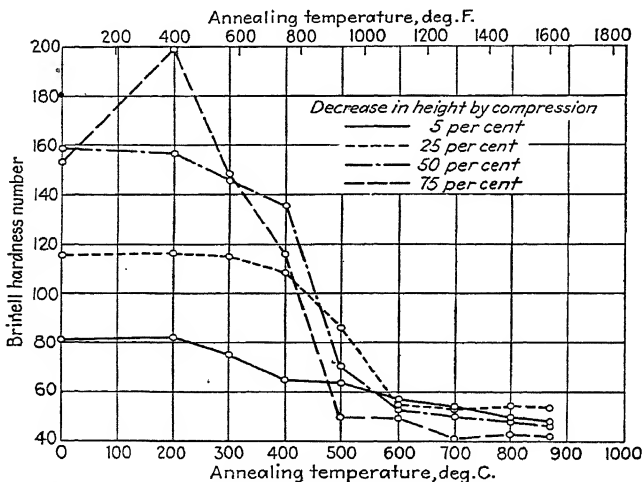
Fig. 74.- –Effect of annealing on the Brinell number of compressed electrolytic iron.   (*Oberhoffer and Oertel.*[408])

genized iron had a Rockwell *B* hardness of between $+10$ and -10.   As previously mentioned in the discussion of the tensile properties of this material, it is probable that the specimens on which these measurements were made were very coarsely crystalline.   The hardness reported by Duftschmid and his collaborators for sintered carbonyl iron was 56 to 80 Brinell.

214. Increase in Hardness by Cold Working.—A comparison of the increased hardness and strength which resulted from cold working of electrolytic iron was made by Freeman and France.[607] They concluded that electrolytic iron (0.06 per cent carbon, 0.002 per cent manganese, 0.010 per cent phosphorus, and 0.012 per cent sulphur) did not harden so rapidly nor increase in tensile

strength so rapidly on cold rolling as did an open-hearth deep-drawing steel.

The increase in hardness of electrolytic iron as a result of different amounts of cold deformation in compression, and the removal of this work hardness by subsequent annealing, are shown in Fig. 74, from the work of Oberhoffer and Oertel.[408] Additional data on the increase in hardness of polycrystalline iron after cold deformation are given in the following discussion of the work hardening of single crystals of high-purity iron.

215. Hardness of Single Crystals of Iron.—Osmond and Frémont[134] and Osmond and Cartaud[148] reported Brinell measurements on different faces of the single crystal previously described in the discussion of tensile tests. The Brinell impressions with a 140-kg. load and a 5-mm. ball were made on three faces of the specimen, both after annealing at 550°C. (1020°F.) and after annealing at 800°C. (1470°F.). The results were as follows:

Type of specimen	Annealed at 550°C. (1020°F.)		Annealed at 800°C. (1470°F.)	
	Diameter of indentation, mm.	Brinell hard-ness	Diameter of indentation, mm.	Brinell hard-ness
Cube face..............	1.540	75	1.642	66
Dodecahedral face........	1.500	79	1.602	69
Octahedral face..........	1.484	81	1.533	76

Osmond and his coworkers thought that these differences between the Brinell hardness of the various crystallographic faces in both series indicated a real difference—the cube faces having the lowest hardness and the octahedral faces the maximum hardness, corresponding to the greater strength in compression which they had observed in tests in which compression was perpendicular to the octahedral face. It is of interest to note also that Osmond and Cartaud made a similar series of hardness determinations on a single crystal of gamma iron from the interior of a cast ingot of Hadfield manganese steel. Although consideration of this material is without the scope of a review of properties of

high-purity iron, the comparison with the results obtained on the alpha-iron crystal is interesting; no significant differences in Brinell hardness were found in comparing the indentations on the cube, dodecahedral, and octahedral faces of the gamma-iron crystal.

Subsequently, Pfeil[736] made a careful and detailed study of the ball indentation hardness of single crystals of iron and of the effect of grain size on hardness. He concluded that there was no difference between the indentation hardness of the various crystallographic faces of the iron crystal; that the size of the crystal in the aggregate of polycrystalline specimens had no measurable effect. Pfeil cut specimens from large crystals of iron and prepared faces on these specimens which represented (*a*) the rhombododecahedral, (*b*) the octahedral, (*c*) the icositetrahedral, and (*d*) the cube faces. He also prepared from the same iron a series of five specimens representing increasing grain size— No. 1 being very fine and No. 5 having crystals about 0.5 mm. in diameter. Table 73 gives the results of Brinell measurements on all of these specimens.

TABLE 73.—BRINELL HARDNESS (10-MM. BALL, 3000-KG. LOAD) FOR ANNEALED SINGLE CRYSTALS AND ANNEALED AGGREGATES*

Material	Brinell Hardness
Single-crystal faces:	
Cube	81.4
Icositetrahedral	80.0
Octahedral	79.6
Rhombododecahedral	85.0
Aggregate No. 1	83.4
Aggregate No. 2	79.6
Aggregate No. 3	81.0
Aggregate No. 4	83.8
Aggregate No. 5	76.4

* Pfeil.[736]

Pfeil considered that the variation in these Brinell numbers (Table 73) was the result of experimental error and, consequently, was insignificant. In support of this belief and in order to obtain a more accurate measure of hardness, he applied Meyer's analysis to his Brinell measurements. Meyer's law is stated as $P = ad^n$, where P is the total load used in making the indentation, a is a constant for a given material and a given ball diameter,

n is a constant depending on the material, and d is the diameter of the indentation. Pfeil found that the values for log a and n were the same for each of the four crystal faces, namely, log $a =$ 1.55 and $n = 2.36$, and that these constants in the case of the five different aggregate sizes were the same for all specimens (log $a = 1.55$ and $n = 2.38$) and nearly identical with those obtained for single crystals. It was concluded, therefore, that single iron crystals obey Meyer's law and further that there is no
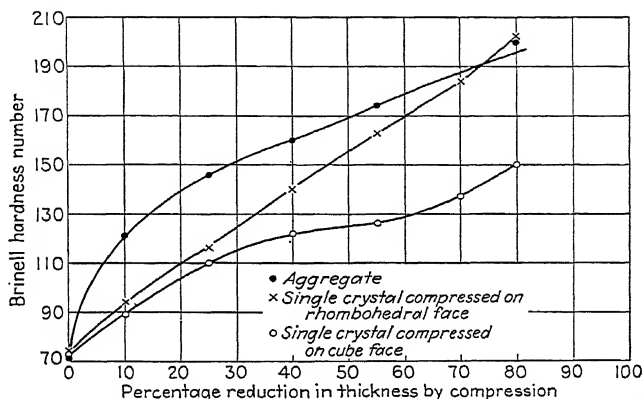
Fig. 75.—Rate of hardening by cold work. Brinell ratio $P/D^2 = 10$. (*Pfeil*.[736])

variation in hardness between the various faces of a single crystal since

. . . it is impossible to believe that this constancy of ball indentation hardness, shown by the constancy of Meyer's a and n, is purely a coincidence, and that, in reality, there are appreciable variations in hardness, these variations being accidentally but exactly neutralized by the inaccuracies introduced by the peculiar shapes of the indents and the method employed in computing the diameters from the measurements.

216. Effect of Cold Working on the Hardness of Single Crystals.—A study was also made by Pfeil[736] of the rate of hardening of single crystals of iron and polycrystalline aggregates of iron after cold working by compressing 10, 25, 40, 55, 70, and 80 per cent. Single-crystal specimens were compressed on faces corresponding to the rhombododecahedral (R), the octahedral (O), the icositetrahedral (I), and the cube (C) faces. It was found that the rate of hardening and the maximum

hardness of single crystals varied with the direction in which the compressive stress was applied. With the lower degrees of deformation differences in the rate of hardening were not pronounced, but the hardness produced by 80 per cent deformation was very different in the four cases tested. The maximum was developed on the *R* face and, in order of decreasing hardness, the sequence of the remaining faces was *O*, *I*, and *C*. Pfeil's results
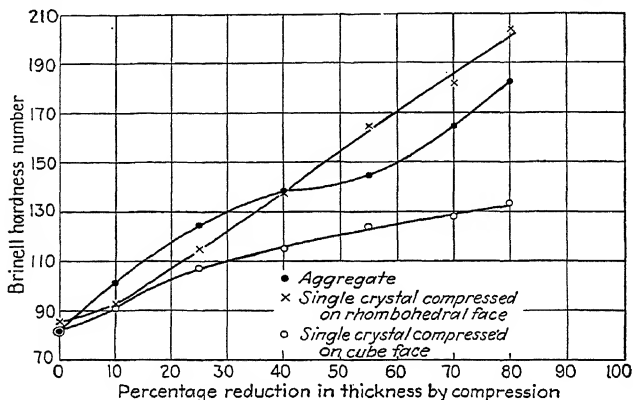
FIG. 76.—Rate of hardening by cold work. Brinell ratio $P/D^2 = 30$. (*Pfeil*.[736])

on the rate of hardening of single crystals are summarized in Table 74 and Figs. 75 and 76.

Gries and Esser[781] determined the relation between Brinell hardness and the degree of cold rolling of polycrystalline iron and single crystals of electrolytic iron. They found that single crystals had the lowest hardness on the cube faces, a higher hardness on the octahedral planes, and the maximum hardness on the rhombododecahedral planes. This is the same sequence of hardness differences that Pfeil found for cold-worked crystals. Gries and Esser also found that the difference between the hardness of the various faces persisted after cold rolling (Fig. 77).

217. Effect of Grain Size.—From a study of a steel containing 0.07 per cent carbon (and other higher carbon steels), Rawdon and Jimeno-Gil[419] concluded that a pronounced increase in grain size was usually accompanied by a decrease in hardness but that grain size was, on the whole, a factor of minor importance in determining hardness.
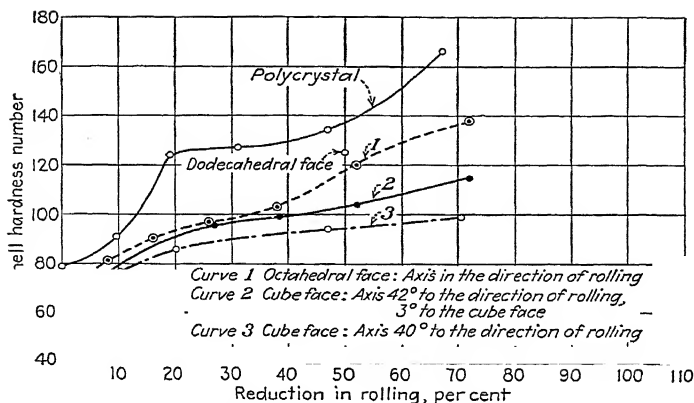
Fig. 77.—Dependence of hardness upon the degree of rolling of polycrystalline iron and of single iron crystals with different orientations. (*Gries and Esser.*[781])

O'Neill[849] made a detailed study of the relation of grain size to hardness of iron. He called attention to the generally accepted belief that for a given testing load the Brinell hardness

TABLE 74.—BRINELL HARDNESS (RATIOS $P/D^2 = 10$ AND 30) FOR THE AGGREGATE AT AND SINGLE CRYSTALS R, O, I, AND C IN SIX STAGES OF COLD WORKING*

Specimen	Ratio P/D^2	Degrees of cold working in compression, per cent					
		10	25	40	55	70	80
AT	10	121	146	160	174	185	200
	30	101	124	138	144	165	182
R	10	94	117	140	163	184	202
	30	92	114	137	164	181	203
O	10	88	115	140	146	179	182
	30	91	114	131	150	176	186
I	10	92	121	138	152	159	163
	30	96	113	130	150	155	151
C	10	89	110	122	128	137	140
	30	91	107	115	124	128	133

* Pfeil.[736]

of a metal increases as the grain size decreases and referred to work by Norbury[526] and by himself[528] on copper and aluminum, which indicated that, although a Brinell number obtained with a given load may vary with different grain size, yet the "ultimate Brinell number" (*i.e.*, the Brinell hardness corresponding to a testing load which produced an indentation of a diameter equal to the diameter of the indenting ball) was constant for aggregates of different grain size. Pomp[332] previously determined the Brinell hardness of a soft iron (containing 0.08 per cent carbon) over a wide range of grain sizes. O'Neill regrouped Pomp's results as follows:

Grains per Sq. Mm.	Brinell Hardness, 5-mm. Ball, 1000-kg. Load
68	83
827	87
1350	89
2310	96
3970	95

O'Neill's own results on specimens of two types of low-carbon iron led him to conclude that:

(*a*) Iron prepared from mild steel by decarburizing in hydrogen, straining, annealing in hydrogen, polishing, and annealing in vacuo has indentation-hardness values independent of the grain size, or of the orientation in the case of single crystals.

(*b*) Normalized Armco iron (carbon, 0.04 per cent), cold worked to various extents and vacuum annealed, has *H* (the ultimate Brinell number) independent of grain size and equal to 58, though constant-load hardness values show variations depending upon grain size.

These variations were noticeable at low testing pressures and showed the fine-grained material to be *softer* than the coarse recrystallized material.

O'Neill confirmed Pfeil's results that the different faces of single crystals of decarburized iron gave the same Brinell values; and these values were the same as for crystal aggregates. However, O'Neill's work showed that the scratch hardness was distinctly different in different directions on crystal faces.

218. Summary of Hardness Data.—The Brinell hardness of electrolytic iron, as deposited, has been reported to be between

180 and 360, depending upon the conditions of deposition. Annealing treatments soften electrolytic iron; Brinell numbers between 50 and 90 have been reported for annealed material. Annealing at 1000°C. (1830°F.) or higher is necessary to produce minimum hardness. Brinell numbers between 60 and 70 have been reported for vacuum-melted electrolytic iron. The limited data which are available indicate that the Brinell hardness of carbonyl or "hydrogenized" iron is about the same as that of vacuum-melted electrolytic iron.

The Brinell hardness of electrolytic iron is increased by cold work but not at so rapid a rate as that of open-hearth steel. Annealing at 500°C. (930°F.) or higher completely removes the hardness caused by cold work. Variation in grain size does not appreciably affect the Brinell hardness. There is no appreciable difference between the ball indentation hardnesses of various crystallographic faces of a single crystal but there appears to be a difference in the rate of work hardening in different directions through a single crystal.

E. RESISTANCE TO IMPACT

Relatively little work has been reported on impact tests of high-purity iron. Tritton and Hanson[585] made Izod tests on the "low-oxygen" material of some iron-oxygen alloys prepared by melting electrolytic iron. The "low-oxygen" ingot was reported to contain 0.08 per cent oxygen and 0.007 per cent phosphorus as impurities. This material had an impact strength of 3.2 ft-lb.

Charpy impact tests on ingot iron containing 0.08 per cent carbon, 0.38 per cent manganese, 0.060 per cent sulphur, 0.066 per cent phosphorus, and traces of silicon were made by Goerens and Hartel.[280] They found the impact strength at about 20°C. (68°F.) to be of the order of 35 to 37 m-kg. per sq. cm. on a 10 × 30 × 160 mm. specimen. Their impact tests were also carried out at higher and lower temperatures (see p. 377).

Impact tests with a Charpy specimen (8 × 10 × 100 mm., keyhole notch 0.65 mm. radius) were made by Bauer[427] on ingot-iron specimens which had been normalized from 900°C. (1650°F.), using a 10 m-kg. testing machine. The mean energy absorbed in a series of duplicate tests was about 12.2 m-kg. per sq. cm.

219. Single Crystals.—Although no quantitative values for impact strength of single crystals of iron were given by Edwards and Pfeil,[553] it is interesting to record their observations on the behavior of single crystals (grown in strip specimens by a strain and anneal method), placed in a vice and given a sharp hammer blow. Large iron crystals were frequently very brittle under such treatment, and in most cases the crystals broke along what appeared to be cleavage planes. In many instances it was possible to obtain fractures in two planes exactly at right angles to each other. A large proportion of the cleavage planes made angles of 45 deg. with the direction of shearing and 90 deg. with the surface of the strip.

F. RESISTANCE TO FATIGUE

220. Fatigue Properties of Commercially Pure Iron.—Fatigue tests of highly purified iron have not been reported. Stanton and Bairstow,[135,462] using alternating tension and compression with axial loading, tested Swedish charcoal iron containing 0.039 per cent carbon, 0.018 per cent phosphorus, traces of manganese and silicon, and no sulphur. They found the maximum limit of the resistance for 1,000,000 reversals at 800 cycles per min. with a ratio of tension to compression of 1.4 to be as follows:

Tension............................	24,800 lb. per sq. in.
Compression........................	17,700 lb. per sq. in.
Range..............................	42,500 lb. per sq. in.

Armco iron containing 0.012 per cent carbon, 0.017 per cent each of silicon and sulphur, 0.014 per cent phosphorus, and 0.07 per cent manganese was tested as received by Gough and Hanson.[511] Specimens in the form of a rotating cantilever were subjected to reversed bending stresses. Two methods of loading were employed: single-point loading to produce uniformly varying bending moment along the length of the specimen, and two-point loading to produce a uniform bending moment over a length of 3 in. Their results for solid specimens are summarized in Table 75. Subsequent experiments on annealed Armco iron subjected to alternate tension and compression in a Haigh machine showed that the fatigue limit for this material definitely exceeded the yield strength; the same result was found with the

TABLE 75.—FATIGUE TESTS OF ARMCO IRON*

Specimen No.	Method of loading	Applied range of stress, lb. per sq. in.	Reversals, millions
2E	Single-point	27,800	4.00 unbroken
2D	Single-point	26,900	27.99 unbroken
2D	Single-point	34,300	0.44 broken
3A	Two-point	28,600	10.7 broken
3B	Two-point	27,300	39.94 unbroken
3B	Two-point	30,600	1.11 broken
3C	Two-point	29,200	3.02 broken

* Gough and Hanson.[511]

same material subjected to reversed torsional stresses in a Stromeyer machine.

The results of a number of investigations on endurance properties of commercially pure iron (most of the tests were made on Armco iron) are summarized in Table 76. Jenkin's[614] tests were made to determine the effect of frequency of reversals on an Armco iron wire 0.104 in. in diameter, normalized 30 min. at 950 to 975°C. (1740 to 1785°F.), and air cooled. Jenkin concluded that the material gains slightly in fatigue strength as the frequency increases, but for most practical speeds the gain is insignificant. The results of Moore and Kommers[443] show the endurance limit of Armco iron determined on the Farmer rotating beam, Upton-Lewis reversed bending, and the Olsen-Foster reversed torsion machines. Additional tests on the Farmer and Olsen-Foster machines were reported by Moore and Jasper.[524]

McAdam[731] also made corrosion-fatigue tests on ingot iron (0.033 per cent carbon, 0.025 per cent manganese, 0.005 per cent phosphorus, 0.036 per cent sulphur, and 0.003 per cent silicon) both as annealed and as heat treated. These tests were made at 1450 r.p.m. The specimens were subjected to corrosion for only 10 days and McAdam suggested that this time was entirely too short to give reliable data. His results are given in Table 77.

A series of tests to determine the effect of cold work on the endurance properties of Armco iron was made by Merrils[573] but failure occurred in only one case; consequently definite values of endurance limits in various conditions cannot be given.

TABLE 76.—FATIGUE PROPERTIES OF COMMERCIALLY PURE IRON

Investigator	Composition, per cent						Endurance limit, lb. per sq. in.	Endurance ratio	Machine used and speed
	C	Mn	Si	S	P	Other elements			
Gough[730]	0.02	....	....	....	....	....	25,300*	0.61	Wöhler rotating beam
Jenkin[614]	0.05	0.44	Trace	0.010	0.016	Ni 0.014 Cu 0.012 / As Cr / 0.021 Trace	35,300 / 37,300 / 38,000		3,000 cycles per min. / 30,000 cycles per min. / 60,000 cycles per min.
Tapsell and Clenshaw[742]	0.02	0.03	Trace	0.034	0.017	Ni Cr / Trace Nil	26,700†		Haigh, alternating tension and compression (mean zero stress); 2400 cycles per min.
Moore and Kommers[443]	0.02	0.03	0.02	0.042	0.005	....	26,000¶ / 23,000¶ / 12,500¶		Farmer, rotating beam / Upton-Lewis, reversed bending / Olsen-Foster, reversed torsion
Moore and Jasper[624]	0.02	0.03	0.02	0.042	0.005	....	24,200 / 26,300 / 20,000 / 13,000		Farmer; 200 r.p.m. / Farmer; 5000 r.p.m. / Farmer; 15,000 r.p.m. / Olsen-Foster

						O₂	N₂				
Moore and Ver[899]	0.02	0.03	0.02	0.042	0.005			22,000‡		0.55	Farmer type
McAdam[442,522]	0.023	0.037	0.005	0.031	0.002			23,600** 25,000			Rotating beam Rotating beam
France[926]	0.02							27,000 26,000			Rotating beam; 1750 r.p.m. Axial loading; 2400 cycles per min.
Gough[562]	0.02							15,700			Stromeyer machine, reversed torsion
Stribeck[533]	0.02	0.03	0.02	0.042	0.005			26,000§			Farmer type rotating beam; 1500 r.p.m.
Hensel and Hengstenberg[1004]	0.02	0.04	0.008	0.043	0.009	0.08	0.004	28,200‖		0.61	Farmer type, 1725 r.p.m.

* For 100,000,000 reversals. The S-N curve became horizontal at 4,000,000 reversals.
† For 10,000,000 reversals.
‡ Box annealed.
§ Specimen 0.3 in. in diameter.
‖ Specimen 0.273 in. in diameter.
¶ Tests on material "as received."
** First specimen "as rolled"; second specimen, quenched in water. The specimens were conically tapered so that the stress was nearly uniform over a length of 1.5 in.

The effect of under-stressing on the endurance limit of hot-rolled Armco iron containing 0.015 per cent carbon, 0.03 per cent manganese, 0.01 per cent silicon, 0.050 per cent sulphur, and 0.007 per cent phosphorus was studied by Kommers.[893] He reported that, with Armco iron having a virgin endurance limit of 26,200 lb. per sq. in., which is above the yield strength of 22,700 lb. per sq. in. and is 60 per cent of the tensile strength (44,300 lb. per sq. in.), stressing for 20,000,000 cycles at the

TABLE 77.—CORROSION-FATIGUE TESTS ON INGOT IRON*

Heat treatment	Endurance limit, lb. per sq. in.		Ratio of endurance limit to tensile strength†	
	In air	In fresh water	In air	In fresh water
Held at 955°C. (1750°F.) for 30 min., furnace cooled..................	21,000	15,000	0.50	0.35
Held at 955°C. (1750°F.) for 45 min., quenched in water, held at 370°C. (700°F.) for 2 hr., furnace cooled..	24,000	21,000	0.55	0.48

* McAdam.[731]
† Based on tensile strength of uncorroded specimens.

endurance limit gave it a new endurance limit of 28,700 lb. per sq. in. or 10 per cent improvement. In the notched test, the endurance limit fell to 18,500 lb. per sq. in., a reduction of 30 per cent. By stressing the notched bar at its own endurance limit its limit was raised 9 per cent to 20,100 lb. per sq. in. Cold-drawn Armco iron of a special grade known as "S. S. Magnetic" (0.04 per cent carbon, 0.02 per cent manganese, 0.03 per cent silicon, 0.032 per cent sulphur, and 0.005 per cent phosphorus) gave an endurance limit of 33,300 lb. per sq. in.

221. Summary of Data on Resistance to Fatigue.—Available data are limited to results obtained from commercially pure irons. Reported results for the endurance limit of Armco iron range from 12,000 to 38,000 lb. per sq. in. depending upon the conditions of test and the size and previous history of the specimen. Endurance limits between 24,000 and 28,000 lb. per sq. in. have been frequently reported.

G. PROPERTIES AT HIGH AND LOW TEMPERATURE

A considerable amount of work has been done on the properties of relatively pure iron (chiefly commercial ingot iron) at high temperatures. In this section attention will be paid to the so-called "short-time" high-temperature tensile tests, and
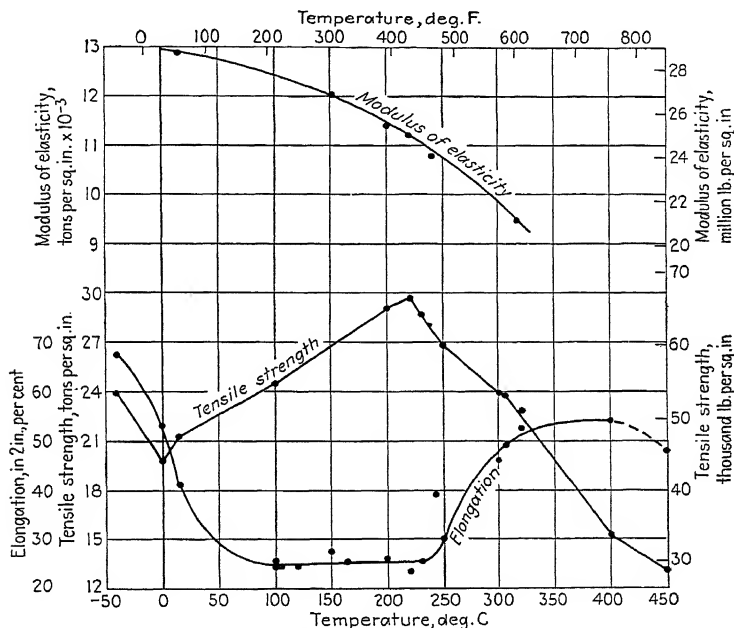
FIG. 78.—Tensile strength, elongation, and modulus of elasticity of Armco iron at various temperatures. (*Lea.*[478])

to high-temperature hardness, impact, and fatigue tests. The "long-time" high-temperature tensile properties, the "creep" properties, will be considered in the section on plastic deformation.

Relatively little work has been carried out on the properties of high-purity iron at low temperatures.

222. Tensile Properties at Elevated Temperatures.—Tensile tests on Armco iron (0.02 per cent carbon, 0.043 per cent manganese, 0.03 per cent sulphur, and 0.013 per cent phosphorus)

were made by Lea[478] at temperatures from -50 to $+1000°$C. (-60 to $+1830°$F.). His results (Figs. 78 and 79) showed a marked increase in tensile strength with decreasing temperature in the range just below atmospheric temperatures, and a progressive increase in elongation with decreasing temperature in the range $+100$ to $-50°$C. (210 to $-58°$F.). The tensile strength increased with increasing temperature from room temperature to a maximum at about 200°C. (390°F.). Over the greater part of this range the elongation remained at the minimum value
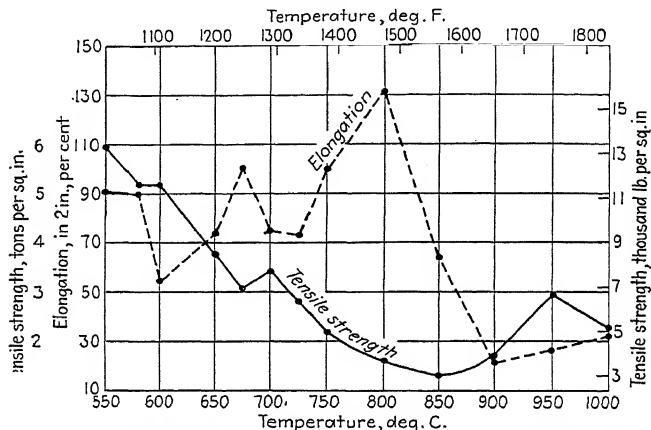
FIG. 79.—Tensile strength and elongation of Armco iron at high temperatures. (*Lea.*[478])

of about 15 per cent. Above 200°C. (390°F.) the tensile strength decreased steadily with increasing temperature up to about 850°C. (1560°F.) after which it apparently passed through a small maximum at 950°C. (1740°F.). The elongation at temperatures above 400°C. (750°F.) varied in a rather erratic manner, but in general remained fairly high (50 to 90 per cent). Lea also determined the effect of temperatures on the modulus of elasticity of Armco iron at temperatures from room temperature to a little over 300°C. (570°F.), as shown in Fig. 78.

The effect of heat and strain on the tensile strength of iron was discussed by Sauveur and Lee.[632] Electrolytic iron with a tensile strength of about 40,000 lb. per sq. in. at room temperature, at first became weaker as the temperature was increased,

exhibiting a strength of only a little above 35,000 lb. per sq. in. at 100°C. (210°F.). As the temperature was increased beyond 100°C. the iron became stronger until it reached a maximum of about 56,000 lb. per sq. in. at 250°C. (480°F.). At temperatures
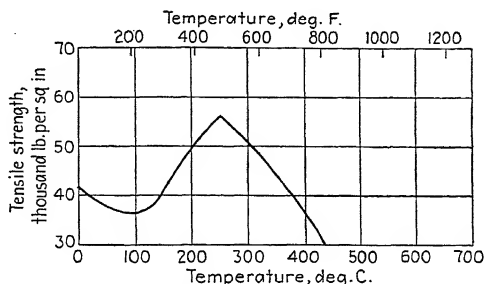
FIG. 80.—Tensile strength of electrolytic iron at various temperatures. (*Sauveur and Lee.*[632])

above 250°C. the strength of iron again decreased, Fig. 80. This temperature of maximum strength corresponds to the "blue-heat" range of increased strength in commercial steels but occurred at a somewhat lower temperature in the electro-
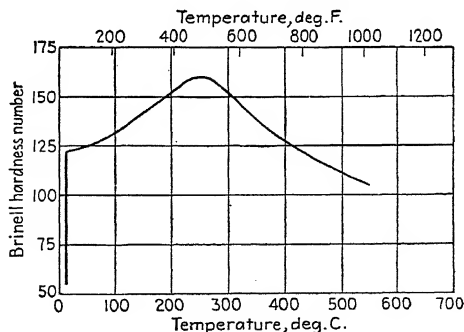
FIG. 81.—Brinell hardness of electrolytic iron at room temperature, after straining at various temperatures. (*Sauveur and Lee.*[632])

lytic iron than in carbon steels. An increase in strength and hardness, similar to that which iron acquires by deformation beyond its elastic range at room temperature, occurs to an even greater degree as a result of plastic deformation of the metal at temperatures up to 250°C. (480°F.) (Fig. 81). The Brinell

hardness, a little over 50 in the annealed electrolytic iron, is
increased to nearly 125 by straining at room temperature and to
about 160 by straining at 250°C. (480°F.); the hardness in the
latter case was measured at room temperature near the broken
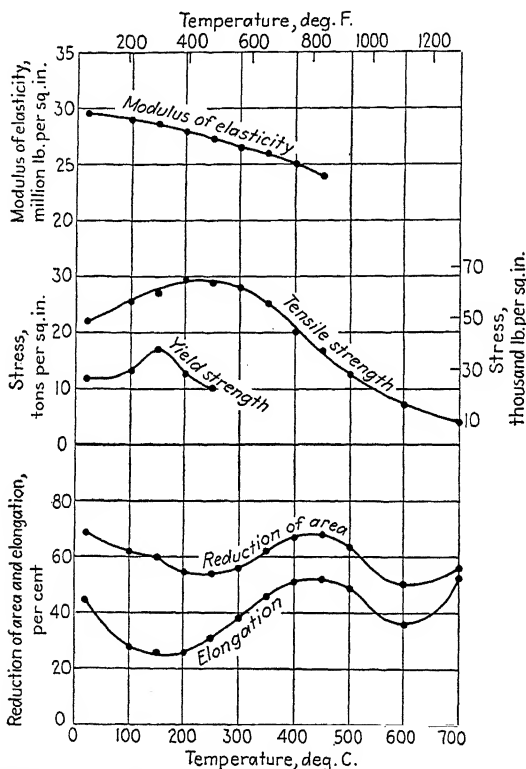
Fɪɢ. 82.—Mechanical properties of Armco iron at elevated temperatures.   (*Tap-
sell and Clenshaw.*[742])

ends of test specimens which had been ruptured at 250°C.
(480°F.).

A rather complete survey of the high-temperature properties
of an Armco iron containing 0.02 per cent carbon, 0.034 per cent
sulphur, 0.017 per cent phosphorus, 0.03 per cent manganese, and
traces of nickel and silicon was made by Tapsell and Clenshaw.[742]
Their results for short-time tensile tests at elevated tempera-
tures, including values for the modulus of elasticity, are given
in Fig. 82.   The tensile strength reached a maximum at about

250°C. (480°F.). Both the reduction of area and the elongation showed minima at two temperatures. In the lower temperature range corresponding to or slightly less than the temperature of maximum tensile strength, the minimum reduction of area occurred at about 250°C. (480°F.) and the minimum elongation at about 150°C. (300°F.). In the higher temperature range the
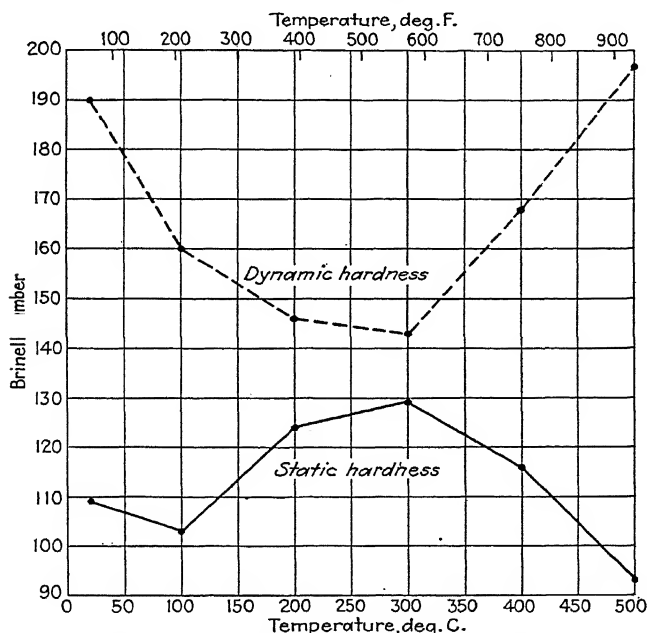
FIG. 83.—Comparison of Brinell numbers obtained in dynamic and static tests at high temperatures. (*Körber and Simonsen*.[569])

minima for both reduction and elongation occurred at approximately 600°C. (1110°F.). Tapsell and Clenshaw commented upon the tendency of Armco iron to contract locally at two or three places when tested at 150 and 200°C. (300 and 390°F.). They attributed this behavior to the probable momentary rise in temperature at that point which first suffers local contracting, this rise in temperature increasing the strength of the material locally and thus causing further local yielding to occur at other points.

223. Hardness at Elevated Temperatures.—The dynamic (impact) hardness of an ingot iron (0.05 per cent carbon, 0.41 per cent manganese, 0.077 per cent phosphorus, 0.032 per cent sulphur, and a trace of silicon) was determined by Körber and Simonsen[569] over a range of temperatures. Their hardness numbers, calculated to equivalent Brinell numbers, present a different picture (Fig. 83) of the effect of temperature on hardness than is given by the usual Brinell numbers obtained from static tests on the same material. The Brinell hardness of the ingot iron under dynamic test (about 190 at 20°C.) decreased with
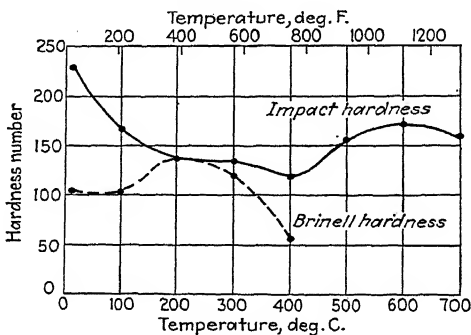
Fig. 84.—Results of hardness tests on Armco iron. (*Tapsell and Clenshaw.*[742])

increasing temperature to a minimum of about 140 at 300°C. (570°F.), while the static Brinell hardness increased from an initial value of 110 at 20°C. (68°F.) to a maximum of nearly 130 at about 300°C. (570°F.), the temperature at which the minimum impact hardness occurred.

Tapsell and Clenshaw[742] also compared the static and impact Brinell values of Armco iron. Their impact hardness numbers were calculated from the formula

$$I = \frac{E}{V}$$

where I = impact hardness number, E = energy absorbed in making the indentation, in meter-kilograms, V = volume of the indentation in cubic centimeters calculated from the diameter. The results of Tapsell and Clenshaw (Fig. 84) present the same general relationship between temperature, impact and static

hardness as did the results of Körber and Simonsen, except that Tapsell and Clenshaw found the maximum static hardness at a somewhat lower temperature (200°C., 390°F.), and the low values for impact hardness extending over a wider range of temperature.

Measurements of the scratch hardness of rather pure decarburized iron at temperatures between −180 and +160°C. (−290 and +320°F.) were made by O'Neill.[849] Figure 85 summarizes his results, representing the mean resistance to the production of a scratch 0.1 mm. wide ($Pw = 0.1$) at the various temperatures, for specimen P 13 R, a cold-rolled polycrystalline
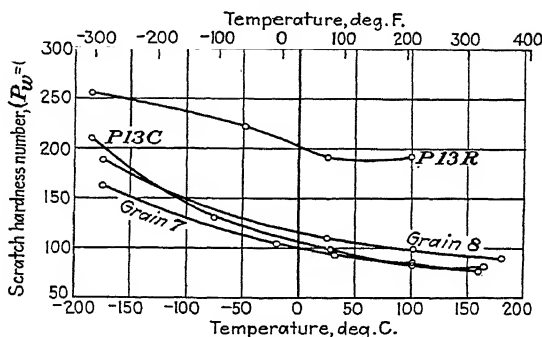
Fig. 85.—Change in scratch hardness with temperature. (*O'Neill*.[849])

aggregate of a carbon-free iron made by decarburizing in hydrogen a mild steel containing 0.44 per cent manganese, 0.02 per cent silicon, 0.028 per cent sulphur, and 0.020 per cent phosphorus; for specimen P 13 C, a polycrystalline aggregate of the same iron but annealed; and for specimens "Grain 8" and "Grain 7," two single-crystal grains, the scratch on the "No. 8" grain being in the [1 1 0] direction on a (1 0 0) face.

224. Impact at Elevated Temperatures.—Charpy impact tests on ingot iron which contained 0.08 per cent carbon were made by Goerens and Hartel[280] over the range of temperature from −75 to +1000°C. (−100 to +1830°F.). They found maxima of energy absorption at about 35 and 600°C. (95 and 1110°F.) and the minimum at about 450°C. (840°F.). Figure 86 represents the values for two different lots of ingot iron.

The effect of temperature on the notched-bar impact tests of a variety of steels was studied by Greaves and Jones.[613] Included

among the materials studied were Swedish bar iron, containing 0.04 per cent carbon, 0.02 per cent silicon, 0.01 per cent manganese, 0.003 per cent sulphur, and 0.039 per cent phosphorus; and Armco iron, containing 0.03 to 0.07 per cent carbon, 0.01 per cent silicon, 0.02 to 0.03 per cent manganese, 0.02 to 0.046 per cent sulphur, 0.013 to 0.017 per cent phosphorus, 0.03 per cent
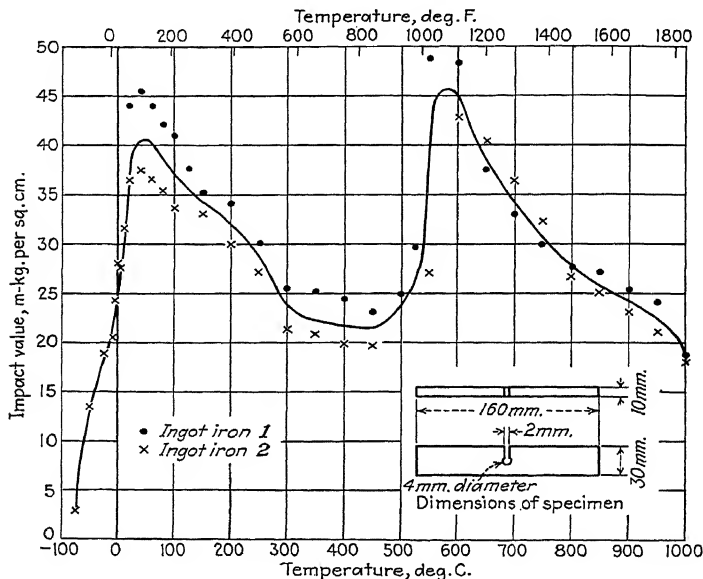
FIG. 86.—Results of impact tests on ingot iron. (*Goerens and Hartel.*[280])

nickel, 0.01 per cent chromium, and 0.07 to 0.11 per cent copper. In tests at various temperatures with Charpy V-notch specimens they found (Figs. 87 and 88) that both of these relatively pure irons showed two maxima for the impact values; the low-temperature maximum occurred at about 0°C. (32°F.) for the Swedish iron and 150 to 250°C. (300 to 480°F.) for Armco iron; the high-temperature maximum for both irons occurred at 700 to 800°C. (1290 to 1470°F.). The minimum energy absorption in impact, between these two maxima, was at 500 to 600°C. (930 to 1110°F.). The two curves in Fig. 88 show that appreciably different results may be obtained from different specimens within

the range of composition of Armco iron. Specimen *A* represents the upper limit of this series for both carbon and sulphur contents, 0.07 and 0.046 per cent respectively; specimen *B* represents the lower limit, 0.03 per cent carbon and 0.002 per cent sulphur.
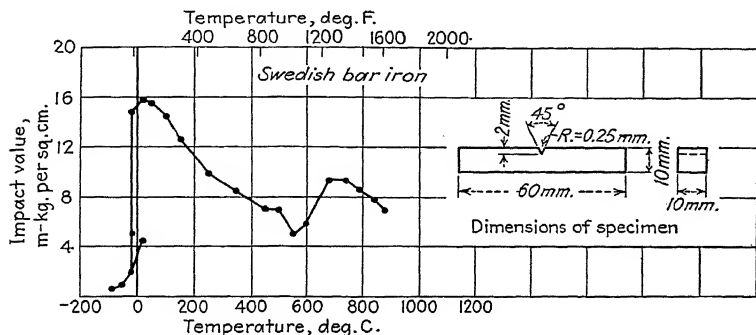
FIG. 87.—Results of notched-bar impact tests of Swedish bar iron at different temperatures. Charpy machine. (*Greaves and Jones.*[613])

The impact values of specimen *A* are consistently lower than those of *B*. In an attempt to correlate high-temperature impact tests with static tests, Greaves and Jones also studied the energy
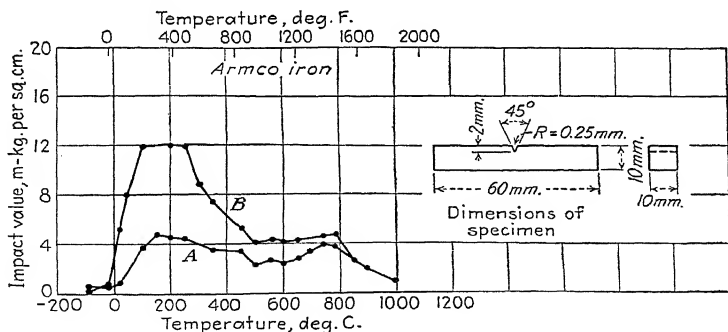
FIG. 88.—Results of notched-bar impact tests of Armco iron at different temperatures. Charpy machine. (*Greaves and Jones.*[613])

absorbed in slow bending tests on notched bars of Armco iron (specimen *A* of Fig. 88) at elevated temperatures as shown in Fig. 89. The curve representing energy absorption still had the two maxima and the intervening marked minimum, as in the

impact tests, but the slower rate of straining shifted the whole
curve towards lower temperatures, so that the minimum of the
curve was at 170°C. (340°F.).
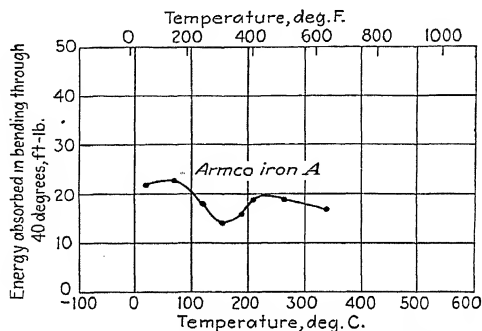
Fig. 89.—Energy absorbed in slow bending tests on notched bars. Specimens
apparently same as shown in Fig. 88. (*Greaves and Jones.*[613])

The same authors also determined short-time high-temperature
tensile strengths of Armco iron. Tests were made at two differ-
ent rates; in one series the duration of the test was 10 min. or
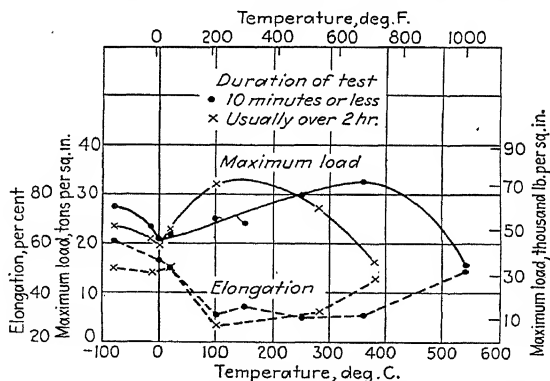
Fig. 90.—Tensile tests on Armco iron "*A*" carried out at different rates
and at different temperatures in special straining apparatus. (*Greaves and
Jones.*[613])

less and in the other series it was usually more than 2 hr. The
maximum tensile strength, after 2 hr., occurred at about 150°C.
(300°F.) under slow straining and at about 350°C. (660°F.) under
the more rapid rate of straining, according to Fig. 90.

Körber and Pomp[615] reviewed the prior work, on impact tests at elevated temperatures, of Charpy,[143] Guillet and Révillon, [193] Goerens and Hartel,[280] Reinhold,[333] Monypenny,[407] Strauss and Fry,[452] Langenberg,[520] Richardson and MacNutt,[578], Goerens,[560] and Mailänder,[571] restricting the
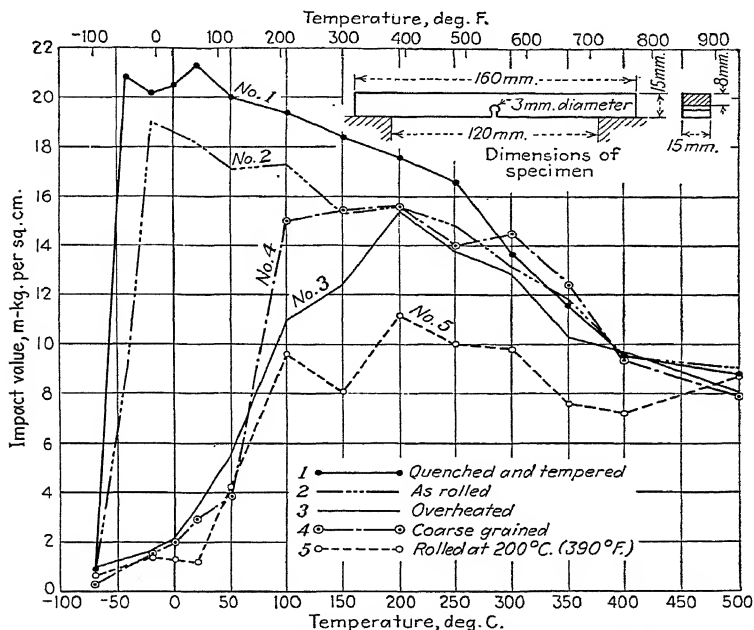
Fig. 91.—Influence of temperature upon the notch brittleness of ingot iron with different previous treatments. (*Körber and Pomp.*[615])

review to the temperature range below 500°C. (930°F.) and calling attention to the fact that the position of the maximum impact strength at low temperatures varied widely (roughly from 0° to 300°C.) depending on the previous treatment of the iron. They also conducted tests on an ingot iron which contained 0.05 per cent carbon, 0.33 per cent manganese, 0.02 per cent silicon, 0.020 per cent phosphorus, and 0.028 per cent sulphur. They made Charpy V-notch impact tests from −80 to +500°C. (−110 to +930°F.). The ingot iron was tested in five different conditions:

1. Quenched and tempered: quenched in water from 950°C. (1740°F.) and tempered 30 min. at 650°C. (1200°F.) in salt.

2. As rolled: in the "as received" condition.

3. Over-heated: 2 hr. at 1250°C. (2280°F.) and cooled in the furnace.

4. Coarsened grain size: annealed 2 hr. at 930°C. (1700°F.), reduced 10 per cent in thickness by rolling, and finally heated 2 hr. at 850°C. (1560°F.).

5. Rolled in the "blue-heat" range: annealed 2 hr. at 930°C. (1700°F.) and rolled with 10 per cent reduction at 200°C. (390°F.).

The results obtained by Körber and Pomp[615] showed (Fig. 91) that these five types of prior treatment, approximately in the
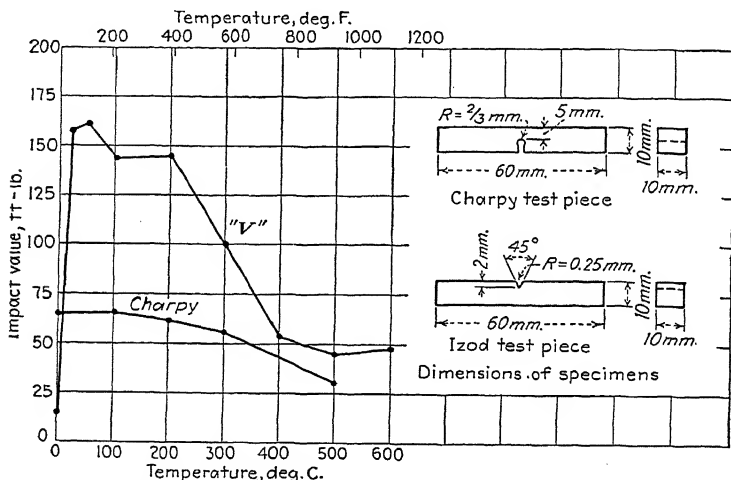
Fig. 92.—Comparison of Charpy and "V" notch for Armco iron. Both types of specimens broken in Charpy machine. Depth of material broken = 0.5 cm. for Charpy-type notch; 0.8 cm. for "V" notch. (*Tapsell and Clenshaw.*[742])

order given, increased the temperature at which the maximum impact strength occurred and decreased the actual energy absorption at the maximum. The quenching and tempering treatment (No. 1) caused the maximum impact strength (20 to 22 m-kg. per sq. cm.) to be reached below room temperature while the hot-rolled specimens (No. 5) reached a maximum of 10 to 12 m-kg. per sq. cm. at 200 to 300°C. (390 to 570°F.).

Impact tests on Armco iron were made by Tapsell and Clenshaw[742] for the two types of specimens shown in Fig. 92. They found a marked maximum in energy absorption over the range

20 to 200°C. (70 to 390°F.) in specimens having the V-notch, a result which corresponded with the work of Greaves and Jones. The Charpy notch bars indicated no marked maximum in energy absorption between 0° and 500°C. (32 and 930°F.) as shown in Fig. 92. Tapsell and Clenshaw called attention to the importance of knowing accurately the temperature of V-notched impact specimens when carrying out tests at what is normally called air temperature, on account of the large variation in impact value between 0° and 100°C. (32 and 210°F.).
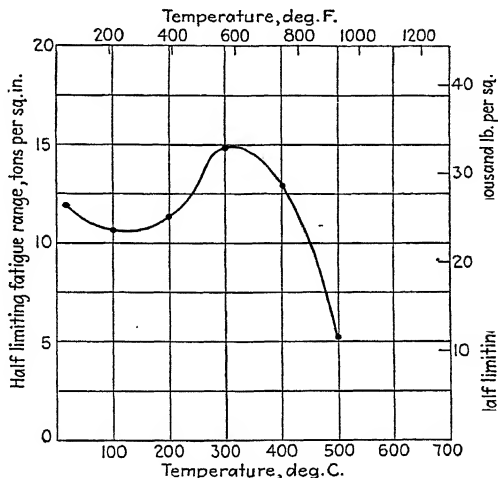
FIG. 93.—Fatigue tests on Armco iron. (*Tapsell and Clenshaw.*[742])

225. Fatigue at Elevated Temperatures.—Fatigue tests on Armco iron containing 0.02 per cent carbon, 0.034 per cent sulphur, 0.017 per cent phosphorus, 0.03 per cent manganese, traces of silicon and nickel, and no chromium were made by Tapsell and Clenshaw,[742] both at room and at elevated temperatures, under alternating tension and compression stresses (mean stress zero) in a Haigh machine operated at a speed of approximately 2400 cycles per min. Results are given in Fig. 93. The tests were made on a 10^7 reversal basis; the estimated fatigue ranges were based only on this number of cycles, and the authors stated that they were not in any way suggested as being the limiting fatigue ranges for an indefinite number of cycles. Their

data showed that the fatigue ranges for mean zero stress, based on 10^7 reversals, were considerably higher between the temperatures 300 and 400°C. (570 and 750°F.) than at room temperature although the limiting creep stresses were falling rapidly at these temperatures. Apparently the time taken to complete 10^7 reversals was too short to allow the effect of creep to manifest itself; the rate of reversal was too rapid.

226. Properties at Low Temperatures.—A Swedish charcoal iron (0.045 per cent carbon, 99.82 per cent iron) at room tem-

TABLE 78.—PROPERTIES OF SWEDISH CHARCOAL IRON AT NORMAL AND AT VERY LOW TEMPERATURES*

Properties	Normal temperature, +15°C. (60°F.)	Liquid-air temperature, −182°C. (−295°F.)	Liquid-hydrogen temperature, −253°C. (−420°F.)
Tensile strength, lb. per sq. in.	52,500	116,500	117,200
Yield strength,† lb. per sq. in ...	41,700	. . . .	117,200
Elongation, per cent............	25	Nil	Nil
Reduction of area, per cent.....	81	. . . .	Nil
Brinell hardness‡..............	101	230	232

* Dewar and Hadfield[122] and DeHaas and Hadfield.[994]
† Reported as yield point.
‡ Calculated from tensile test.

perature had a tensile strength of 44,800 lb. per sq. in. and 20 per cent elongation and as cooled in liquid air at −182°C. (−295°F.) a strength of 85,000 lb. per sq. in. with no elongation, according to Dewar and Hadfield.[122] Hadfield[129] later reported tests on six Swedish charcoal irons (0.04 per cent carbon) at liquid-air temperatures which gave tensile strengths of 85,000 to 121,000 lb. per sq. in. DeHaas and Hadfield[994] recently carried out tensile tests on a Swedish charcoal iron (0.03 per cent carbon, 0.01 per cent silicon, 0.04 per cent manganese, 99.89 per cent iron) at the temperature of liquid hydrogen (−252.8°C.) and calculated the Brinell hardness from the maximum stress obtained in the tensile tests. The results obtained by Dewar and Hadfield and by DeHaas and Hadfield are summarized in Table 78.

Guillet and Cournot[468] made Brinell hardness tests on electrolytic iron at low temperatures with the following results:

Temperature		Brinell hardness
°C.	°F.	
+ 20	+ 68	80
− 20	− 5	77
− 80	−110	77
−110	−165	95
Liquid air		269

In coarsely crystalline specimens broken in tension impact at −10 to −170°C. (+14 to −275°F.), the course of the fracture was transcrystalline, and there was practically no deformation of the crystals broken at the lower temperatures, according to the recent work of Sauerwald and Pohle.[856]

Heindlhofer[1056] applied a torsion test to cold-rolled bars, $1\frac{3}{64}$ in. in diameter and 1 in. in length, of purified iron at low temperatures, down to liquid-air temperatures, and found that the bars could be twisted through approximately four complete revolutions before rupture by shear occurred. It was therefore concluded that the range in which plasticity of iron in torsion disappears lies below liquid-air temperature. However, abrupt changes in the plasticity of iron were observed in other tests, at −20 to −30°C. (−5 to −20°F.) for an impact test, and at about −155°C. (−245°F.) for a tensile test. The precise temperature ranges varied to some extent with the material, with its previous treatment, and with the shape and size of the specimen, but the differences in temperature between the three types of tests were unmistakable. However, after applying stress analysis to these data, Heindlhofer concluded that each of the three types of test involves a different combination of stresses and that the indicated temperature for the loss of plasticity is a function of that particular combination of stresses. "The 'plasticity' of a metal depends upon the mode of action of the stresses which produce the deformation, and therefore upon the method of test."

227. Summary of Data on the Effect of Temperature on the Mechanical Properties of Iron.—The effect of temperature on

the different mechanical properties of iron is best summarized by reference to Figs. 78 to 93 inclusive. In general, an increase in temperature within the range from -250 to $+1000°$C. (-420 to $+1830°$F.) is accompanied by a decrease in tensile strength, yield strength, and Brinell hardness and by an increase in elongation and reduction of area. However, the change in properties with increasing temperature is not always regular; in the temperature range above $0°$C. a maximum in the strength and hardness curves is shown at temperatures within the blue-heat range; Charpy impact tests show two maxima, in the vicinity of $100°$C. ($210°$F.) and $700°$C. ($1290°$F.), but the actual temperatures are appreciably affected by relatively small changes in composition.

H. PLASTIC DEFORMATION

Brittle materials rupture when subjected to applied stresses which exceed the elastic limit but many metals, including iron, can be appreciably deformed without rupture. According to Kenyon and Mehl,[1010] the first visible effect of cold plastic deformation on the microstructure of iron is the production of slip bands on a polished surface. If the deformation is a sufficient amount, the grains become distorted and elongated, and this appearance, unlike slip bands, is not changed by repolishing and re-etching. This effect can only be detected after considerable cold reduction. Macroscopically, cold-deformed iron exhibits, on fairly smooth or polished surfaces, a peculiar phenomenon that has been variously designated as Hartmann or Lüders lines, "worms," and "stretcher strains." When formed in tension, these markings are surface depressions resulting from local yielding; when formed in compression, they are local elevations on the surface. Deformation does not produce these markings on iron which has been previously cold worked an amount sufficient to prevent a sharp yield point. Sudden or impact deformation produces the so-called impact twins or Neumann bands. These twins differ from twins in face-centered metal in that they frequently exhibit irregular or serrated outlines; apparently iron forms no strain-anneal twins.

228. Mode of Deformation of the Iron Crystal.—The mechanism of the first stages of plastic deformation of iron, before the crystalline grains become noticeably distorted and elongated,

has been a subject of extended investigation.   Early studies of polycrystalline material led to controversial conclusions and it was only after single-crystal specimens were available that authoritative data on plastic deformation were obtained.   One of the first studies of plastic deformation in a single crystal of iron was made by Taylor and Elam[689] who stated that previous results were, in general, unreliable "partly because the largest crystals available were too small for accurate experiment, partly because workers have assumed that planes of slip coincide with crystal planes . . . , but chiefly because the analysis of strain has not been carried out in a systematic manner so as to obtain all information possible from external measurement of strained crystals."   Taylor and Elam's conclusion that slip in iron could be likened to the movement of a large bundle of rods which slide on one another was not entirely acceptable to subsequent investigators.   Pfeil[681] concluded that slip in an iron crystal occurs on icositetrahedral planes, the movement on a plane taking place in the direction of the trigonal axis parallel to that plane.   Gough's extended study[714,780,886,999] of single crystals led him to conclude that, in general, deformation of a body-centered cubic lattice such as that of alpha iron occurs by a process of duplex slip on two crystallographic planes, $(1 1 0)$ and $(1 2 3)$ or $(1 1 2)$ and $(1 2 3)$.   Other authors,[998,1025] however, are convinced that slip in alpha iron occurs only along the $(1 2 3)$ planes.   In some recent work by Akulov and Raewsky,[1042] in which a single crystal of iron was subjected to continuous pressure in the $[1 0 0]$ direction, above the elastic limit, it was found that periodically alternating sliding occurred along the $(1 0 0)$, $(0 1 0)$, and $(0 0 1)$ planes.   Most of the investigators agree with the theoretical conclusion, as expressed by Mathewson,[1018] that "plastic deformation of a crystal occurs in the direction of a line of closest atom packing by block movement along planes of the densest atom packing on which the stress intensity has reached the highest value . . . "; the difficulty seems to be in the experimental determination of the orientation of the slip planes.

In discussing the results of severe plastic deformation, Mathewson[1018] stated that

. . . as the slipping proceeds in any crystal the process tends to become more complicated owing to a rotation which accompanies the block

movement and consequent increase of stress in other eligible slipping directions. Large amounts of deformation therefore bring many different slip planes into play, and in the case of ordinary polycrystalline material the process is further complicated by inhomogeneity of the force field at the grain boundaries. Hardening accompanies deformation of this character perhaps owing to an increased resistance to slip through the minute blocks of crystalline material which in moving past one another have developed slight differences in orientation. . . . In spite of the complex mechanism of the slipping process, the crystalline particles of metal worked into a given form by continued application of stress in some prescribed manner finally become forced into positions closely approximating a definite and characteristic preferred orientation. Simple stretching brings a cube face diagonal [1 1 0] into the axis of the rod with a radial disposition of a corresponding set of cube edges [0 0 1] in the different crystals. In cold-drawn wires [1 1 0] also occurs as the fiber axis. Under compression a body diagonal [1 1 1] and to a lesser extent a cube edge occurs in the direction of compression with a cube face diagonal in the radial position. In torsion the cube face diagonal and to some extent the [1 1 2] direction becomes the fiber axis with the body diagonal tangential. Cold rolling brings a face diagonal into the direction of rolling and a cube face into the plane of rolling.

Between about 900 and 1400°C. (1650 and 2550°F.) gamma iron exists in a face-centered cubic pattern.

No detailed study has been made of the slip planes and directions brought into play by hot working pure iron in this range of temperature, but there is little doubt that the mechanics of deformation are analogous to those observed in aluminum, copper, and other face-centered metals. . . . In the face-centered cubic metals only the planes of closest atom packing, the octahedral planes (1 1 1), function as slip planes and the slip occurs in the direction of one of the three cube-face diagonals representing close-packed rows of atoms on the given plane. Four families of octahedral planes are available for this purpose. In single crystals under tension stress, slip starts on the set of octahedral planes for which the computed shear stress is a maximum and continues on these planes until rotation of the lamellae brings an equal load on another set of octahedral planes. After a short period of extension by slipping on both sets of planes the crystal usually breaks with a wedge-shaped fracture. Pursuing the analogy with face-centered cubic metals (cold) still further, hot rolling of iron above 905°C. (1660°F.) might be expected to develop preferred orientation of the crystalline particles with the normal to a trapezohedral plane,

(1 1 2), approximately parallel to the direction of rolling and a dodec-ahedral plane, (1 1 0), parallel to the plane of rolling. Subsequent cooling below the A_3 point would produce some form of reorientation depending upon the relationship between the two sets of crystal axes established during the transformation. No accurate details of this process are yet available.[991]

The effect of increasing temperature, within the range of stability of a given allotropic form, is to increase both the ease and capacity for plastic deformation of a pure metal. This is due to the decreased elastic limit at higher temperatures and to the increased atomic mobility which tends to decrease or to prevent the development of work hardening in the material. The presence of alloying elements or impurities in a metal may cause irregularities in the temperature–plastic deformation relation due to solubility phenomena particularly in intergranular material; for example, "red shortness" in iron is usually ascribed to the presence of sulphur. Increasing the temperature through the range of an allotropic transformation naturally is accompanied by a change in the deformation characteristics.

229. Effect of Rate of Strain.—Time is also a factor in plastic deformation; in the ordinary processes of rolling, drawing, or forging, deformation is rapidly accomplished through the application of relatively large stresses; on the other hand, metals will creep, *i.e.*, will undergo slow but progressive deformation under lighter loads provided the load is continuously applied for long periods of time.

The time factor in the plastic deformation of iron at elevated temperatures has been recognized in recent years as a most important consideration, in that the permissible loads in engineering structures at elevated temperatures are very largely determined by the total permissible change in dimensions over relatively long periods of time, frequently periods of several years.

The high-temperature strength of iron as considered in previous sections was concerned only with tension tests made under conditions of relatively rapid loading of the specimens, rates of loading comparable with those employed in tension tests at normal temperatures. These rapid-loading tests at elevated temperatures are the so-called "short-time" high-temperature tests. Such tests, however, do not present a complete picture

of the strength of iron at high temperatures. If the load be maintained over a relatively long period of time, a specimen of iron at an elevated temperature may continue to elongate over a period of weeks, months, or years. This behavior is the so-called "creep" phenomenon.

Studies of the behavior of metals under prolonged loading at elevated temperatures have received increasing attention in recent years, but relatively little work has been done on high-purity iron. The few data that are available have as a rule
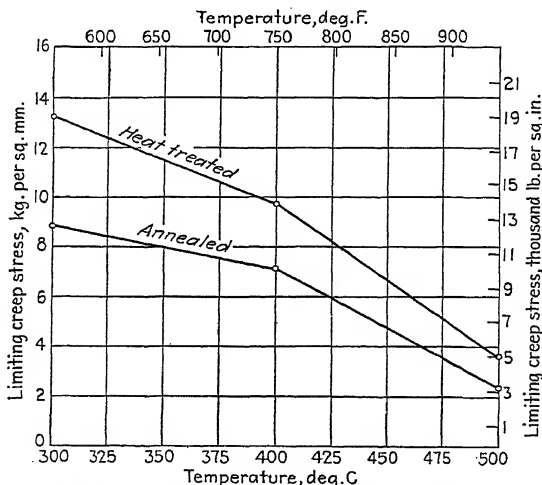
Fig. 94.—Limiting creep stress of annealed and heat-treated iron ·at elevated temperatures. (*Pomp and Dahmen.*[737])

been secured by different types of creep tests and are difficult of comparison.

Cournot and Sasagawa[601] determined "creep limits" for a mild steel containing 0.04 per cent carbon. Their tests were of extremely short duration (1.5 hr.) and compare more with present-day "accelerated creep tests" than with the more usual long-time tests. Cournot and Sasagawa determined the highest load which, at the selected temperature, failed to produce measurable creep over the 1.5-hr. period of test. The smallest rate of strain detectable in their work was of the order of 2×10^{-4} mm. per hr. (8×10^{-6} in. per hr.) on a specimen 100 mm. (4 in.)

long. With this value as the criterion for designating a creep limit Cournot and Sasagawa gave the following values for the creep limit of the 0.04 per cent carbon steel:

Temperature, °C.........	350	400	500	600
Temperature, °F.........	660	750	930	1110
Creep limit, lb. per sq. in.	44,000	28,400	11,400	5700

Pomp and Dahmen[737] used an accelerated creep test and arbitrarily selected as the creep limit that stress which produced a rate of creep of 0.001 per cent between the third and sixth hour of the loading period. They reported the results given in Fig. 94 as representing the creep limit of a steel which contained 0.046 per cent carbon, both as annealed and after quenching from 950°C. (1740°F.) in water and tempering at 550°C. (1020°F.).
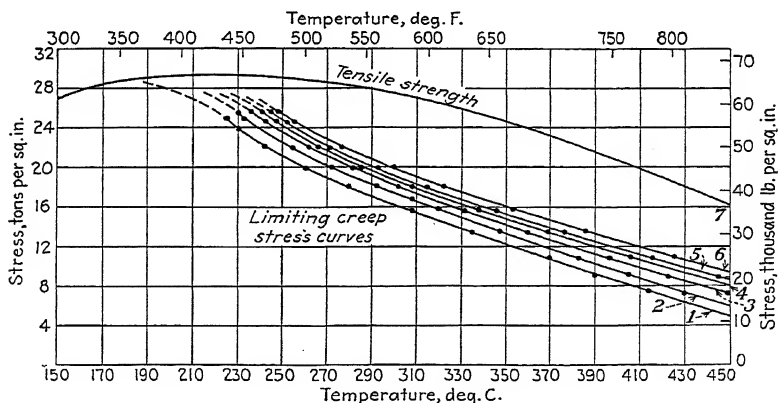
Fig. 95.—Relation between ordinary tensile strength and limiting creep stress in Armco iron. No. 1 is the limiting-creep-stress curve. The other curves show the stress giving the steady rate of stretch in inches per day for the estimated time of fracture.

Curve	Stretch, in.	Time, days
2	0.001	300
3	0.005	60
4	0.010	25
5	0.025	8
6	0.075	2 to 3

Curve 7 gives the tensile strength. (*Tapsell and Clenshaw.*[742])

The relations found by Tapsell and Clenshaw[742] between short-time tensile tests and creep tests lasting from 50 to 70 days on Armco iron are summarized in Fig. 95. The limiting creep stress as given by Tapsell and Clenshaw represents a rate of creep of less than 1×10^{-4} in. per day.

A creep (extension-time) curve at 400°C. (750°F.) for Armco iron loaded at 6700 lb. per sq. in. was given by Baumann.[873] This curve showed the following initial deformation and creep:

Initial extension	0.00026
Extension after 250 hr.	0.00052
Extension after 750 hr.	0.00057
Extension after 1500 hr.	0.00063
Extension after 2500 hr.	0.00067

Pomp[902] gave "limiting creep stresses" (Table 79) for 0.06 per cent and 0.07 per cent carbon ingot irons as approximated by Pomp and Dahmen's accelerated creep-test methods.

TABLE 79.—LIMITING CREEP STRESS OF INGOT IRON*

Mark	Composition, per cent						Limiting creep stress, lb. per sq. in.		
	C	Si	Mn	P	S	Cu	300°C. (570°F.)	400°C. (750°F.)	500°C. (930°F.)
A1	0.06	Trace	0.43	0.016	0.029	0.17	15,500	11,200	3600
B1	0.06	Trace	0.46	0.031	0.040	0.21	19,700	9,900	3400
C1	0.07	Trace	0.42	0.021	0.046	0.14	17,600	13,800	1600
E6	0.07	Trace	0.42	0.025	0.039	0.18	23,100	14,200	1400

† Pomp.[902]

In a study of the applicability of the Rohn method for determining the creep characteristics of metals, Austin and Gier[1045] reported creep tests on a very pure iron in which only the following impurities were recognized: 0.001 per cent carbon, 0.004 per cent silicon, 0.002 per cent manganese, 0.008 per cent sulphur, 0.002 per cent phosphorus, 0.016 per cent oxygen, and a trace of copper. The Rohn test depends upon an arrangement such that the dimensional change of the creep specimen, supporting a constant load, automatically controls the heating current of the furnace. As the specimen elongates, the temperature is gradually lowered until it finally reaches a value at which the constant
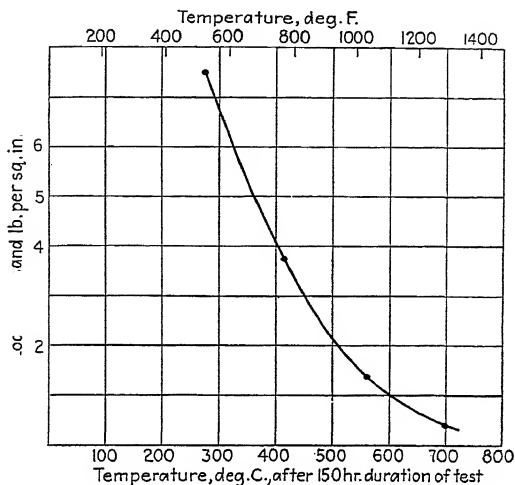
FIG. 96.—Stress-temperature relation in iron after 150 hours duration of test.
(*Austin and Gier.*[1045])
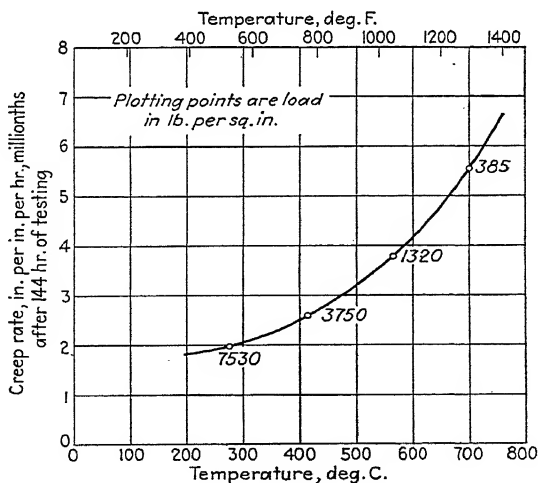
FIG. 97.—Relation between temperature, load, and rate of creep of iron after 144 hours duration of test. (*Austin and Gier.*[1045])

load is supported with no further elongation.   The temperature therefore asymptotically approaches a constant value.

Austin and Gier recorded in Fig. 96 the relation between load and the constant temperature approached at the end of the 150-hr. periods of the Rohn test as applied to their "pure" iron. Figure 97 gives the rates of creep calculated from the rate of change of the temperature after the iron had been loaded as indicated for 144 hr.

It should be noted that most of these data on the time factor in the plastic deformation of high-purity iron at elevated temperatures were obtained from tests which fall in the category of "accelerated creep" tests.   The longer tests of Tapsell and Clenshaw and of Baumann presumably yield more dependable information than do the accelerated tests, but it cannot be stated definitely that even the longest test available, 2500 hr., truly depicts the creep characteristics of the material.

I. AUTHORS' SUMMARY

Reported values for the tensile strength of relatively pure iron vary all the way from 14,000 to more than 100,000 lb. per sq. in., depending upon the physical condition and grain size, as well as the composition of the material.   An increase either in purity or in grain size tends to lower the tensile properties.   The tensile strength of polycrystalline electrolytic iron which has been vacuum-melted and annealed, is probably within ±5000 lb. of 40,000 lb. per sq. in.

The modulus of elasticity of high-purity iron, according to the limited data available, is about the same as that of Armco iron.   For polycrystalline material in the annealed state, Young's modulus would be 30,000,000 lb. per sq. in. as determined by extrapolation.   This is intermediate between the values obtained for different directions in a single crystal of Armco iron, 19,000,000 lb. per sq. in. in the [1 0 0] direction and 41,000,000 lb. per sq. in. in the [1 1 1] direction.

The strength in compression also varies with the orientation; it is least when compressed on the plane of a cube face.   The elastic limit in compression of a single crystal, according to Pfeil,[681] varied from 5200 to 6600 lb. per sq. in., depending upon the orientation.

Brinell hardness numbers between 50 and 90 have been reported for electrolytic iron in the annealed condition and between 60 and 70 for similar material which has been vacuum-melted. The hardness number of iron is materially increased by the presence of impurities or added elements; it may be increased two- or threefold by cold working; changes in grain size exert relatively little effect on the results of hardness determinations; recent data indicate that there is no appreciable difference in the hardness of different faces of a single crystal of iron.

Data for the resistance to impact and to fatigue of high-purity iron are not available at present. Our knowledge of the effect of high and low temperatures on the mechanical properties of relatively pure iron is based almost entirely upon tests of Armco iron. The mechanical properties of this material vary in an irregular manner with changes in temperature, but, in general, an increase in temperature above $-250°C.$ ($-420°F.$) is accompanied by a loss of strength and hardness in iron.

Iron is capable of plastic deformation and, within the range of stability of each of the allotropic forms, both the ease and the capacity for plastic deformation are increased by an increase in temperature. The presence of alloying elements or impurities may cause irregularities in the relation between temperature and plastic deformation as a result of solubility phenomena.

Additional data are desired for the mechanical properties of high-purity iron particularly in the form of single-crystal specimens.

CHAPTER XI

HEAT TREATMENT AND AGING

Quenching—Annealing—Aging—Authors' Summary

Heat treatment involves the heating and cooling of a solid metal at controlled rates, the object being the alteration of its properties. Heat-treatment operations are of two general types, quenching, where the heated metal is rapidly cooled, and annealing, where the heated metal is cooled slowly.

A. QUENCHING

The quenching of iron-carbon alloys from suitable temperatures results in hardening of the metal but, as carbon is usually considered the effective agent, high-purity iron would not be expected to exhibit this type of hardening. However, the evidence whether quenching does or does not produce hardening in high-purity iron such as electrolytic iron, is somewhat contradictory.

230. Hardening of High-purity Iron by Quenching.—Boynton[139] determined the relative hardness of the constituents of iron and steel after various treatments, by means of the Jagger microsclerometer. The hardness was measured by the number of revolutions of a diamond point necessary to drill to a depth of 0.01 mm. The results indicated that quenching more than doubled the hardness of melted electrolytic iron, according to the following data:

Treatment	Hardness, Number of Revolutions Necessary to Penetrate 0.01 Mm.
Annealed, unetched....................	505
Annealed, etched.....................	502
Melted, annealed, unetched............	460
Melted, annealed, etched..............	463
Melted, quenched from 850°C. (1560°F.)	998
Melted, quenched from 1300°C. (2370°F.)	982

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However, Bauer and Schneider[429] could not detect any increase in the Brinell hardness of electrolytic iron after quenching and concluded that the increase reported by Boynton was the result of cold work on the surface of the metal. Their determinations of the tensile strength of plates and rods of electrolytic iron showed quenching from various temperatures to be without effect on the strength, according to the results presented in Table 80. On the other hand, Ludwik and Scheu[620] found that heat treatment of previously annealed electrolytic iron at temperatures below 200°C. (390°F.) did not affect the irregularity in the tensile-strength curves, which they termed the yield strength, but that heat treatment at temperatures above 200°C. caused the irregularity in the curves to disappear.

TABLE 80.- –EFFECT OF QUENCHING ON THE BRINELL HARDNESS AND TENSILE STRENGTH OF ELECTROLYTIC IRON*

Quenching temperature		Brinell hardness	Tensile strength, lb. per sq. in.	
°C.	°F.		Plates	Bars
Annealed	. . . .	58.4	36,800	34,000
620	1150	. . . .	. . . . . .	35,700
650 to 660	1200 to 1220	56.8	. . . . . .	34,300
720 to 730	1330 to 1345	55.2	36,700	
800 to 810	1470 to 1490	57.7	. . . . . .	33,700
820 to 840	1510 to 1545	56.9	36,400	
850 to 860	1560 to 1580	58.3	37,400	33,300
1000	1830	59.3	33,700	
1050 to 1060	1920 to 1940	. . . .	36,400	34,300
1100	2010	. . . .	. . . . . .	34,000
1200	2190	56.9		
1250	2280	58.7		

* Bauer and Schneider.[429]

On the assumption that carbon is essential to the formation of martensite, Bain[544] stated that a pure iron cannot be hardened by quenching, at least not to an extent comparable with that obtained by cold working. Rawdon, in the discussion of Bain's paper, stated that electrolytic iron had been hardened by intensely heating a spot on a polished plate of electrolytic iron (carbon, 0.02 per cent) with a high-potential spark from a

pencil of the same iron.   Only a small volume of iron was heated, consequently the subsequent cooling was extremely rapid. The degree of hardness obtained, as shown by the scratch test, was far greater than could be obtained by cold working.   The results indicated the possibility that, contrary to the general belief, carbon is not fundamentally essential in the hardening of iron by quenching.   Sauveur and Chou[856A] found that drastic quenching of electrolytic iron, from temperatures above the A_3 transformation, produced a Widmanstätten or martensitic structure.   Mehl and Smith[1064] occasionally obtained a Widmanstätten figure in quenched electrolytic iron which contained only 0.004 per cent of carbon.

231. Hardening of Commercially Pure Iron by Quenching.— That there is appreciable change in the hardness and other properties of commercially pure iron as a result of quenching was indicated by the data reported by Kenyon[787] for basic open-hearth ingot iron (Table 81).   Whiteley[751] also found that the Brinell hardness of basic open-hearth ingot iron (0.035 per cent carbon) increased with increasing quenching temperature,

TABLE 81.—EFFECT OF FORGING PRACTICE AND HEAT TREATMENT ON THE PROPERTIES OF BASIC OPEN-HEARTH INGOT IRON*

No.	Treatment	Yield strength,† lb. per sq. in.	Tensile strength, lb. per sq. in.	Elongation in 2 in., per cent	Reduction of area, per cent	Brinell hardness	Impact value, ft-lb. per sq. in.
1	As forged, finished cold.....	26,900	43,800	41.8	75.6	101	503
2	As forged, finished hot......	19,100	42,200	44.7	77.3	90	422
3	Finished hot, annealed 25 hr. at 900°C. (1650°F.), cooled slowly..................	18,300	41,000	47.0	70.6	82	695
4	Finished hot, air cooled from 940°C. (1725°F.)..........	19,300	43,500	45.0	73.7	92	390
5	Finished hot, water quenched from 940°C. (1725°F.).....	30,300	47,000	36.2	70.0	110	452
6	Finished hot, water quenched from 940°C. (1725°F.), tempered at 650°C. (1200°F.)..	20,800	42,700	41.8	71.1	94	276
7	Finished hot, annealed 2.5 hr. at 900°C. (1650°F.), cooled moderately slowly (faster than No. 3)..............	18,900	42,900	43.2	72.8	87	163

* Kenyon.[787]
† Reported as yield point.

from 89 for the untreated metal to 116 for the same metal quenched from 980°C. (1795°F.). Dickie[820] found that the Brinell hardness of annealed basic open-hearth ingot iron, originally 79.5, was increased to 173 by quenching from 710°C. (1310°F.).

232. Summary of the Effect of Quenching.—The information in the literature, although somewhat contradictory, seems to indicate that quenching as ordinarily practiced in heat treatment does not measurably affect the mechanical properties of high-purity iron, although unusually severe quenching, where the iron is cooled at an extremely rapid rate from a very high temperature, does result in hardening. The hardness of commercially pure iron, such as ingot iron, is increased by quenching.

B. ANNEALING

Annealing operations are employed to decrease the hardness, to remove strains, or to refine the structure of iron. The hardness and strained condition may be the result of cold working or, in the case of electrolytic iron, may be due to the presence of occluded hydrogen.

233. Early Work on Annealing of Cold-worked Iron.—Although data are plentiful on the effect of annealing the commercial forms of iron, little has been published on the annealing of high-purity iron for removing the effects of cold work.

Portions of test bars of iron, which contained about 0.2 per cent impurities and which had been strained in tension, were annealed by Stead.[82] At 500°C. (930°F.) there was a slow recrystallization; between 600 and 750°C. (1110 and 1380°F.) rapid recrystallization occurred. Goerens[240] investigated the effect of annealing on cold-worked commercial iron and steel and found that there was little effect until a critical annealing temperature was reached. At this temperature, which varied between 520 and 580°C. (970 and 1075°F.) for different compositions, there was a sudden reversion of the properties to those of the original unworked metal. The action characteristic of any annealing temperature was exerted during the first few minutes of annealing, only small further changes being produced by prolongation of the annealing time.

A critical range of deformation was observed by Sauveur.[265] With deformation greater or less than the critical range, little

or no crystal growth occurred upon annealing at 650°C.(1200°F.), whereas deformation within the critical range caused the formation of abnormally large crystals. Robin[290] investigated the effect of annealing on cold-worked mild steel and found that the crystal size reached a maximum during annealing at temperatures between 700 and 750°C. (1290 and 1380°F.), being smaller with either higher or lower temperatures. The results obtained by Chappell[301] on basic open-hearth ingot iron and Swedish wrought iron may be summarized as follows:

1. Plastic strain in practically every degree produced recrystallization in iron on annealing below the A_3 temperature.

2. The temperature of recrystallization became lower with increased amount of deformation. The incipient stages started as low as 350°C. (660°F.) and with sufficient time recrystallization was complete at 700 to 750°C. (1290 to 1380°F.).

3. Practically carbon-free iron, after plastic deformation at any temperature below 900°C. (1650°F.), recrystallized when annealed. Under certain conditions the crystals developed to abnormal sizes.

The recrystallization temperature of cold-worked ingot iron was found by McAdam[382] to be between 480 and 800°C. (900 to 1470°F.). In this range the metal behaved as if it contained recrystallization nuclei, the number depending upon the degree of deformation. A further study[392] indicated that for cold-compressed ingot iron there was little tendency to coalesce or to recrystallize below 790°C. (1450°F.). Above that temperature the tendency to coalesce increased rapidly with increasing temperature, reaching its maximum at 870°C. (1600°F.).

234. Work of Oberhoffer and Associates on Annealing Cold-worked Iron.—Probably the outstanding work on the relation between the amount of cold work, the annealing temperature, and the resultant grain growth in high-purity iron is that of Oberhoffer and Oertel.[408,574] Cylinders of electrolytic iron were deformed by compression, the amount of deformation being measured as the percentage reduction in height. These deformed cylinders were annealed at temperatures between 200 and 870°C. (390 and 1600°F.) for 15 min. to 25 hr. The results, some of which are reproduced in Table 82, indicated that the temperature at which recrystallization began depended on the amount of previous deformation, being lower with increasing deformation. With severe deformation the grain growth was slow at annealing

temperatures up to 700°C. (1290°F.) but was rapid at higher temperatures; with mild deformation the grain growth, once started, was rapid. The hardness of the specimens (Table 83) could not be judged by the microstructure and appeared to be independent of grain size, indicating the occurrence of a physical change not visible to the eye.

TABLE 82.—RECRYSTALLIZATION ON ANNEALING OF COLD-WORKED ELECTROLYTIC IRON*

Anneal-ing time	Annealing temperature		Grain size in μ^2 for reduction by compression of			
	°C.	°F.	5%	25%	50%	75%
15 min....	400	750	100,000	100,000	100,000	100,000
	450	840	100,000	100,000	†	†
	500	930	100,000	100,000	370	480
	600	1110	32,000	11,000	530	900
	700	1290	51,000	40,000	2,260	2,104
	800	1470	86,000	50,000	5,270	2,500
	870	1600	98,000	85,000	25,000	39,000
1 hr......	400	750	100,000	100,000	100,000	100,000
	450	840	100,000	100,000	†	†
	500	930	100,000	100,000	730	580
	600	1110	42,500	12,000	1,400	1,600
	700	1290	56,000	18,500	3,000	2,200
	800	1470	59,000	65,000	47,300	3,400
	870	1600	65,000	90,000	52,000	49,000
10 hr.....	400	750	100,000	100,000	†	†
	500	930	†	18,000	900	460
	600	1110	38,000	16,500	1,200	530
	700	1290	43,000	25,000	1,800	600
	800	1470	64,000	41,000	2,600	97,000
	870	1600	86,000	51,500	97,000	99,000

* Oberhoffer and Oertel.[408]
† Recrystallization begins.

In an investigation of the recrystallization of commercial irons and other metals, Oberhoffer and Jungbluth[482] found that commercial iron showed maximum grain growth after 10 per cent deformation and subsequent annealing at 700 to 800°C. (1290 to 1470°F.). To determine if this anomaly was characteristic of

TABLE 83.—EFFECT OF ANNEALING ON THE BRINELL HARDNESS OF
COLD-WORKED ELECTROLYTIC IRON*

Annealing temperature		Brinell hardness after reduction in area of				
°C.	°F.	0%	5%	25%	50%	75%
Not annealed		....	80.7	115.3	159.4	152.4
200	390	....	81.2	117.0	157.6	(199.3)?
300	570	....	74.7	115.2	146.0	148.4
400	750	....	64.4	108.3	135.3	116.5
500	930	....	62.5	87.0	70.4	49.3
600	1110	....	57.7	54.5	51.8	49.1
700	1290	....	53.0	52.4	50.0	41.0
800	1470	....	49.3	52.9	48.4	42.4
870	1600	....	48.5	52.4	45.4	41.2
950	1740	42.4				

* Oberhoffer and Oertel.[408]
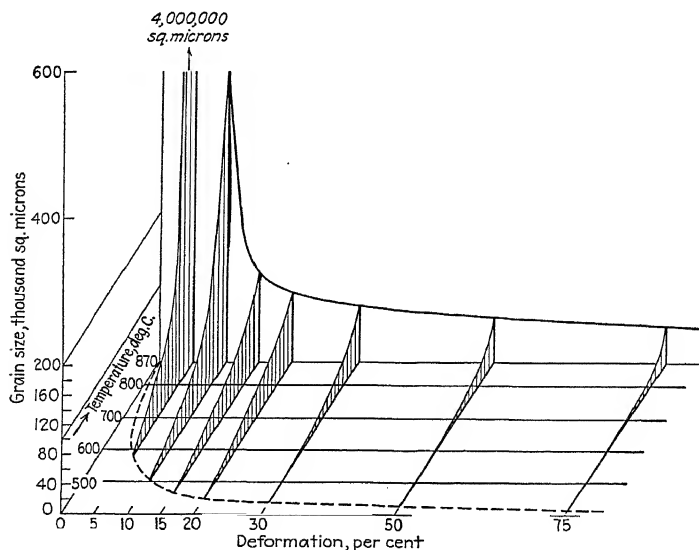
FIG. 98.—Relation between amount of deformation, annealing temperature, and resulting grain size in electrolytic iron. (*Oberhoffer and Oertel.*[574])

iron or was an effect of the impurities in the commercial iron, Oberhoffer and Oertel[574] repeated their work with electrolytic iron but with smaller intervals of deformation. The results (Table 84) showed no maximum grain growth within the range of critical deformation, indicating that Oberhoffer and Jungbluth's results were probably due to impurities present ·in commercial iron. Their results were also presented in the form of a three-dimensional diagram (Fig. 98).

235. Later Work on Annealing Cold-worked Iron.—The recrystallization of deformed ingot iron (iron content about 99.8 per cent) was investigated by Fischer.[507]   If the temperature of deformation was below the A_3 point, recrystallization, which was visible without a microscope, took place between 590 and 910°C. (1095 and 1670°F.) and occurred at a maximum rate at 730°C. (1345°F.).   At this temperature at least 2 hours' annealing was necessary to obtain noticeable recrystallization; with 6 hours' annealing, recrystallization was completed.   The greatest crystal growth occurred when the material was stressed to, or just above, the elastic limit.   Such material showed very little strength and was particularly deficient in toughness as indicated by the notched-bar impact test.

TABLE 84.—RECRYSTALLIZATION OF COLD-WORKED ELECTROLYTIC IRON*

Annealing temperature		Grain size in μ^2 after deformation in compression of						
°C.	°F.	5%	10%	15%	20%	30%	50%	75%
300	570	95,000	95,000	120,000	95,000	95,000		
400	750	94,000	130,000	95,000	95,000	95,000		
500	930	140,000	160,000	95,000	95,000	95,000	†	78
600	1110	170,000	16,000	18,000	16,000	3,000	1,250	135
700	1290	97,000	68,000	40,000	36,000	11,600	4,000	2,700
800	1470	150,000	150,000	73,000	61,000	40,000	13,200	11,600
870	1600	4,000,000	400,000	98,000	94,000	75,000	62,000	49,000

* Oberhoffer and Oertel.[574]
† Recrystallization begins.

Freeman[660] observed that cold-rolled electrolytic iron showed incipient recrystallization when annealed at 400°C. (750°F.) and underwent marked recrystallization as revealed by the

microstructure and by the change in physical properties (Figs. 99 and 100) after 30 minutes' anneal at 500°C. (930°F.). Increase in carbon content increased the temperature necessary to start recrystallization, cold-rolled sheet steel (0.06 per cent carbon) showing incipient recrystallization at 600°C. (1110°F.). Sauveur and Lee[632] found that annealing at temperatures above 425°C. (795°F.) was necessary to soften cold-worked electrolytic iron,
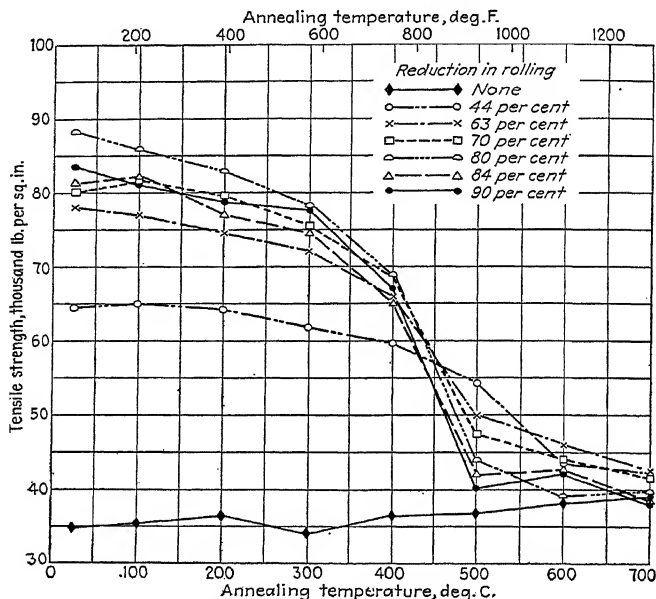
Fig. 9.—Effect of annealing on the tensile strength of cold-rolled electrolytic iron. (*Freeman.*[660])

but Wever and Pfarr[1037] found, as did Freeman, that recrystallization of cold-worked electrolytic iron or ingot steel begins at 400°C. The results of Tammann and Moritz,[1031] shown in Fig. 101, indicated that most of the hardness of electrolytic iron after cold working was removed by annealing between 500 and 600°C. (930 and 1110°F.) but that annealing at 800°C. (1470°F.) or above was necessary for complete recovery.

X-ray investigation by Kurdjumow and Sachs[894] of the structure of electrolytic iron and of soft iron, after rolling and after
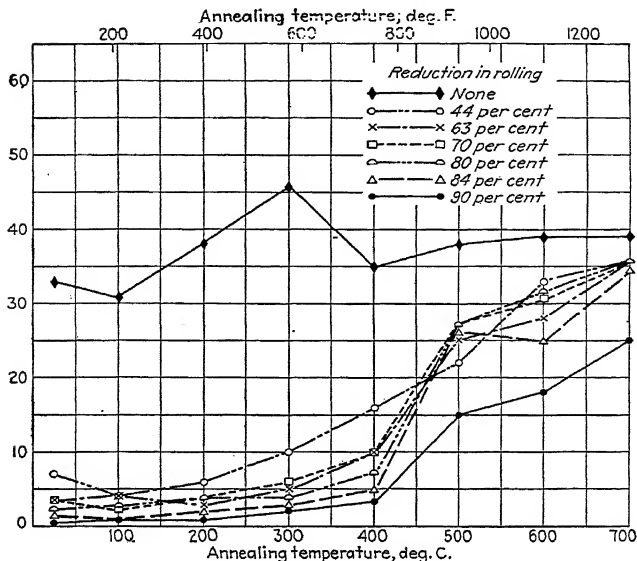
Fig. 100.—Effect of annealing on the elongation of cold-rolled electrolytic iron.
(*Freeman.*[660])
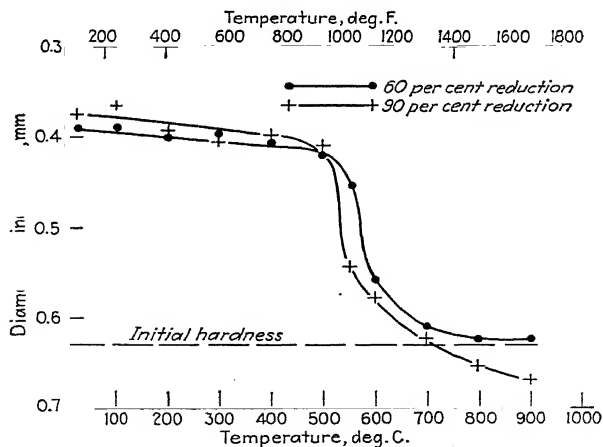
Fig. 101.—Effect of annealing on the indentation hardness (2.37 mm. ball, 20.1 kg. load) of cold-worked electrolytic iron. (*Tammann* and *Moritz.*[1031])

recrystallization, indicated that the structure produced by rolling was not entirely lost upon recrystallization but persisted even after heating above the A_3 transformation and slowly cooling.

When cold-worked basic open-hearth ingot iron was heated there was a slight evolution of heat at 690°C. (1270°F.) according to Krivobok.[617] As this heat effect did not recur on cooling or on reheating of the sample, it apparently represented the release of energy introduced during cold working. Satô[938] also found that heat was released when cold-worked iron was annealed, the temperature of the maximum heat effect being about 550°C. (1020°F.) for cold-rolled electrolytic iron and about 570°C. (1060°F.) for basic open-hearth ingot iron.

The results of a photomicrographic study of the recrystallization of cold-worked electrolytic iron by Krivobok[674] may be summarized as follows: After cold work, the orientation of the grains of the metal as a whole is preserved, distortion affecting only slight volumes of the crystalline material. The distorted portions take the form of narrow streaks. When the metal is heated the distorted portions tend to revert to the stress-free condition. The material in the strain markings, the most distorted material, crystallizes first, the metal between the strain lines being unaffected and structureless. As recrystallization continues the grains penetrate the structureless mass and finally the whole metal is completely recrystallized. The time between cold working and annealing is a factor in the recrystallization; with annealing following immediately after cold working complete recrystallization occurred, whereas with lapse of time between deformation and annealing recrystallization was incomplete.

The time factor in the softening of deformed metals by annealing was investigated by Sauerwald and his associates.[939,1024] In the latter investigation, cylindrical samples of copper and hydrogen-purified mild steel were compressed at different temperatures by a falling hammer, annealed at the temperature of compression, and then quenched; the Brinell hardness was determined at room temperature. By this method the effects of the recovery of crystalline properties (Erholung) and of recrystallization could be separated. Recovery without recrystallization had a greater softening effect with iron than with copper. It was not determined whether, with sufficient time, complete softening may be effected by recovery without recrystal-

lization. It was concluded that proposed theories of recrystallization must be modified to take into consideration the time factor.

Numerous theories of the mechanism of recovery and recrystallization in deformed metals have been proposed, based in many cases on studies of the phenomena in nonferrous metals as well as in iron, but applicable to metals in general. Some of the more important papers in regard to the theoretical aspects of recrystallization are those by Dehlinger,[770,819,877] Alterthum,[461,915] Gross,[563] Masing,[521,623] van Arkel and Koets,[746] Tammann[864,909] and Tammann and Crone.[910] Czochralski[704] reviewed the theories and developments in recrystallization studies up to 1921 and Dehlinger[819] brought the review up to 1927.

236. Effect of Annealing on the Hardness and Structure of Cathode Iron.—That the characteristic brittleness of electrolytic iron as deposited is removed by annealing and that the removal of brittleness is accompanied by an evolution of hydrogen were matters of early knowledge. Cailletet[30] in 1875 showed that as much as 284 times its volume of hydrogen was evolved from electrolytic iron during annealing with accompanying loss in hardness.

The relation between annealing temperature, time, and the hardness and crystal structure of electrolytic iron was investigated by Cournot[411] using test pieces annealed in a gas-fired furnace and in a fused salt bath. The original structure of the cathode iron was partially altered by annealing between 650 and 750°C. (1200 and 1380°F.); at 850°C. (1560°F.) and above, it was completely altered to the normal ferrite structure. This complete alteration of the structure did not coincide with the attainment of minimum hardness; 1 hour's anneal at 850°C. (1560°F.) sufficed to complete the change in structure but 4 hr. at that temperature were not sufficient to produce minimum hardness. Two hr. at 950°C. (1740°F.) or 1 hr. at 1050°C. (1920°F.) were necessary for complete annealing (Table 85).

The heat treatment of electrolytic iron deposited to build up undersized or worn steel parts was studied by MacFadyen.[406] If the metal was annealed at a temperature above the A_3 point for a short time (30 min. at 950°C. [1740°F.]), the sharp dividing line between the steel and the electrolytic iron disappeared, the

TABLE 85.—EFFECT OF ANNEALING ON THE BRINELL HARDNESS OF
ELECTROLYTIC IRON*

Annealing temperature		Initial hard-ness	Brinell hardness after indicated time at annealing temperature						
°C.	°F.		10 min.	20 min.	40 min.	1 hr.	2 hr.	4 hr.	6 hr.
650	1200	164	161	160	161	159	155		
750	1380	164	155	157	153	152	144	140	136
850	1560	164	135	120	115	107	95	92	
950	1740	164	103	100	96	88	84		
1050	1920	164	88	87	84	83	83		

* Cournot.[411]

needle-like crystals of the deposit altered to ferrite grains which
interlocked with the grains of the steel. Attempts to chip off
the deposited iron caused portions of the base metal to come away
with the deposit. At annealing temperatures below A_3 the
line of demarcation between the base metal and the deposit
remained sharp. Case hardening the deposit at 850°C. (1560°F.)
without previous annealing failed to obliterate the junction line;
with case hardening at 950°C. (1740°F.) the junction line was
less sharp but still discernible. Case hardening at 850°C.
followed by annealing at 950°C. also failed to obliterate the
junction line, whereas a short anneal at 950°C. followed by case
hardening at 850°C. gave a structure which showed no discon-
tinuity between the base metal and the deposit.

The effect of annealing temperature on the hardness, structure,
and rate of loss of hydrogen in electrolytic iron was investigated
by Pilling.[485] The iron used contained 0.005 per cent carbon,
0.001 per cent manganese, 0.005 per cent phosphorus, 0.022 per
cent silicon, 0.005 per cent sulphur, 0.11 per cent hydrogen, and
a trace of copper. Specimens were annealed in air, in an electric
tube furnace. At the higher temperatures a thin scale of oxide
was formed but this was ground off in preparing the surface for
the hardness measurements. The scleroscope hardness remained
constant for annealing temperatures up to 200°C. (390°F.) (Fig.
102), but an anneal at 300°C. (570°F.) increased the hardness
from 26.4 to 45.3. Material annealed at 200°C. cracked when

hammered but that annealed at 300°C. deformed satisfactorily
under the hammer. The hardness decreased with increasing
annealing temperature to a minimum at 795°C. (1460°F.).
There was a slight increase in hardness of material annealed at
900°C. (1650°F.) but the increased hardness was lost by annealing
at 945°C. (1730°F.).   The rate of evolution of gas was measured
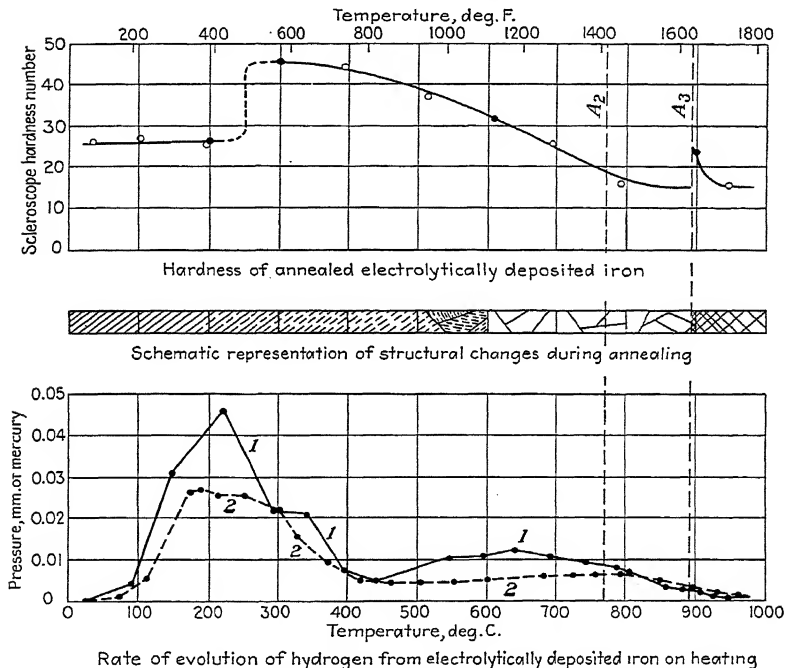
Fig. 102.—Relation between annealing temperature and the hardness, struc-
ture, and hydrogen evolution of cathode electrolytic iron.   Curves 1 and 2 are
duplicate runs of the same iron.   (*Pilling.*[485])

by the pressure when the temperature of specimens in a vacuum
was slowly raised to about 1000°C. (1830°F.).   The average
rate of increase in temperature between 100 and 800°C. (210 and
1470°F.) was 13°C. (23°F.) per min.   The rate of evolution of
gas increased rapidly above 100°C. (210°F.) to a maximum at
about 200°C. (390°F.), decreased to a minimum between 400 and
500°C. (750 and 930°F.), increased slightly with temperature to

about 700°C. (1290°F.), then decreased to zero at about 950°C. (1740°F.) as is shown in Fig. 102. There was little change in microstructure below 600°C. (1110°F.), at which temperature a distinct coalescence into larger units of similar crystallographic orientation began. This primary recrystallization was completed at 700°C. (1290°F.). Above 900°C. (1650°F.) there was a complete structural change, the new structure resembling that of iron which had been fused.
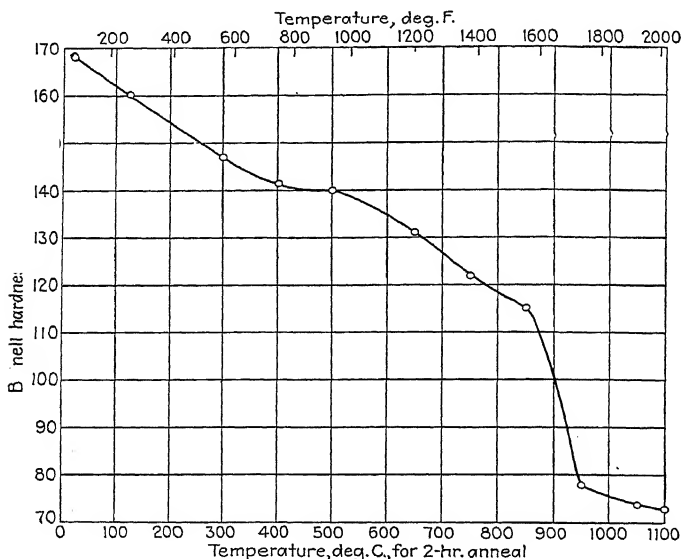
Fig. 103.—Effect of annealing on the hardness of cathode electrolytic iron. (*Cazaud and Hugues.*[600])

The hardness of "Beve" electrolytic iron was found by Cazaud and Hugues[600] to decrease rapidly for annealing temperatures between 850 and 950°C. (1560 and 1740°F.), with little further decrease at higher annealing temperatures up to 1100°C. (2010°F.) (Fig. 103). They stated that tensile strength and impact values substantiated this finding but did not give sufficient information concerning their data to permit proper interpretation.

Reed[627] annealed strips of electrolytic iron at temperature intervals of about 40°C. (70°F.) and tested for brittleness by

bending the annealed strips. The specimens remained brittle after annealing at temperatures below 345°C. (650°F.); specimens annealed at that temperature were malleable and could be bent through an angle of 180 deg. No change in microstructure was observed to accompany the increase in ductility. The very fine-grained structure of the iron, as deposited, assumed a polyhedral shape upon annealing at 675°C. (1245°F.); annealing at 790°C. (1450°F.) caused little further change in structure.

Electrolytic iron after heating to 1000°C. (1830°F.) had the granular structure of ordinary iron, according to Burgess and Watts.[142] Storey[317] found that the structure of cathode iron changed completely to that of ordinary ferrite when the specimens were heated for 1 hr. at 910 to 915°C. (1670 to 1680°F.), but that no change in structure was detectable after one hour's heating at any temperature below 875°C. (1605°F.). When heated above the A_3 range, fine-grained cathode iron changed more readily to the ferrite structure than did coarse-grained iron. The grain size of the ferrite corresponded roughly with the structure of the cathode metal, *i.e.*, fine-grained ferrite was produced from a fine-grained cathode metal.

Annealing in hydrogen as a method of removing sulphur from electrolytic iron was studied by Oma.[845] Electrolytic iron from a sulphate bath contains as much as 0.03 per cent sulphur according to Oma; about 0.001 per cent is present as sulphide from the anode material, the remainder being sulphate from the electrolyte. By heating at temperatures above 800°C. (1470°F.) in hydrogen most of the sulphur could be removed, the rate of removal being a function of time, temperature, and particle size. The following data illustrate the influence of these three variables on the removal of sulphur from electrolytic iron:

<div align="center">

Effect of Temperature (50-mesh powder)

</div>

0.013 per cent sulphur removed in 2 hr. at 800°C. (1470°F.)
0.028 per cent sulphur removed in 2 hr. at 950°C. (1740°F.)

<div align="center">

Effect of Time (50-mesh powder)

</div>

0.027 per cent sulphur removed in 2 hr. at 900°C. (1650°F.)
0.030 per cent sulphur removed in 4 hr. at 900°C. (1650°F.)

<div align="center">

Effect of Particle Size

</div>

50-mesh powder....... 0.028 per cent sulphur removed in 2 hr. at 950°C.
30-mesh powder....... 0.020 per cent sulphur removed in 2 hr. at 950°C.
 5-mm. diameter...... 0.012 per cent sulphur removed in 2 hr. at 950°C.

237. Grain Growth in Annealing.—Annealing electrolytic iron at temperatures below 900°C. (1650°F.) did not affect the crystal structure, according to Stead and Carpenter,[295] other than to cause slight recrystallization of the surface which had been cold worked in preparing the specimens. They found that heating at 910 to 915°C. (1670 to 1680°F.), followed by cooling to room temperature, produced very coarse crystals, the change in crystal structure being very abrupt as it was completed after 2 or 3 sec. at the high temperature. The new crystals were equiaxed, but if the annealing temperature was raised to 930°C. (1705°F.) radial crystals appeared and at higher temperatures displaced the equiaxed crystals entirely. Coarse crystals were obtained only when the iron was cooled slowly through the Ar_3 point; quenching from temperatures above A_3 resulted in a finely crystalline structure. The formation of abnormally large crystals occurred only in thin sheets of electrolytic iron, about 0.01 in. in thickness. Once the coarse crystals were formed, no heat treatment below the Ac_3 point, without previous cold deformation, would refine or alter them. Stead and Carpenter suggested that if a certain number of alpha-iron nuclei are present after heating above Ac_3, these act as centers of rapid recrystallization when the Ar_3 transformation occurs, with coarse recrystallization resulting. When heated to a temperature considerably above the Ac_3 point the alpha-iron nuclei are completely destroyed and recrystallization upon passing through the A_3 transformation results in a fine-grained structure.

238. Theories of Grain Growth.—Jeffries[379] in 1916 advanced the hypothesis, to explain grain growth, that when a metal is heated a "germinative" temperature is reached at which adjacent grains coalesce and form larger ones. This temperature is affected somewhat by the rate of heating; rapid heating requires a higher temperature to initiate grain growth, but growth is more rapid. High resistance to grain growth, either inherent in the metal or resulting from the presence of impurities, necessitates a higher germinative temperature but results in the formation of coarse crystals, on account of the rapid growth at the higher germinative temperature. In the case of material which has been cold worked the size of the grains before deformation influences the size of the grains formed during annealing; large grains before deformation result in large grains after annealing. Uniform

grain size with a temperature gradient, or uniform temperature with deformation, or a combination of the two, results in the formation of large grains at the germinative temperature.

Howe[373] elaborated Jeffries' explanation and summed up the influences affecting grain growth as follows: Grain growth is favored and the germinative temperature is lowered by grain fineness, by grain-size contrast, by prior plastic deformation, and by increase in temperature. Grain growth is opposed, and consequently the germinative temperature is raised, by obstructions such as cementite or slag and by grain-size equalization or decrease of grain-size contrast. The rate of growth increases with the difference in the absorption power between adjoining grains, whether this is due to a difference in their temperature, their size, or their prior plastic deformation. It further increases with temperature, with critical grain fineness and with prior plastic deformation. The rate of growth decreases as the grain size increases.

In discussion of the papers of Jeffries[379] and of Howe,[373] Ruder stated that annealing at 1000°C. (1830°F.) of powdered electrolytic iron, which had been compressed, resulted in the formation of large crystals, but that re-annealing at 1300°C. (2370°F.) caused the large crystals to break up, producing material with a fine grain structure. Jeffries' explanation of this was that at 1000°C. the small gamma-iron grains formed germinant centers for alpha iron which absorbed the small germinant grains as the allotropic change occurred, with large alpha-iron grains resulting; at 1300°C. the iron was composed of large gamma-iron grains which broke up into alpha iron from several centers at the same time and thus caused a small-grained structure of alpha iron. It may be mentioned here that although Ruder found that powdered, compressed electrolytic iron showed grain growth when annealed at 1000°C., Sauerwald[488] found a temperature of 1100°C. necessary to initiate grain growth in similar material. Howe[388] considered the evidence of the inheritance by alpha iron of the gamma-iron grain size so abundant as to cast doubt on Jeffries' explanation and offered as a simpler explanation the grain growth by metal coarsening as in the case of the growth of large crystals by the method of Stead and Carpenter. Ruder in the discussion of Howe's paper[388] stated that, if a specimen of strained ingot iron was annealed at 1000°C.

(1830°F.), a fine-grained structure resulted and that annealing at 1300°C. (2370°F.) caused the gamma grains to grow forming a coarse structure, the reverse of the results with powdered iron. The coarse-grained ingot iron from the 1300°C. anneal, when re-annealed at 1000°C., had a much coarser structure than after the first anneal at 1000°C. Ruder inferred that either the large-grained material did not refine to the same extent as did the fine-grained material on passing through the Ac_3 point, or that there is a grain inheritance by the gamma iron from the ferrite. From further study on the recrystallization of ingot iron and steel as well as from the results of previous investigators on electrolytic iron, Jeffries[390] reached the following conclusions regarding the recrystallization of iron:

1. The ferrite grain size in pure iron is not inherited from the grain size of the mother austenite.

2. The only structural feature generally inherited from the austenite of hypo- and hypereutectoid steels on cooling through the transformation ranges is the position of the excess ferrite or cementite at the austenite grain boundaries resulting sometimes in networks which outline the old austenite grain boundaries.

3. The austenite grain boundaries themselves are nearly always effaced in steels and pure iron during the Ar_3 transformation.

4. The grain refining of steel and iron is brought about by the combined effect of non-inheritance of the transformation products during either heating or cooling.

5. In general, in both iron and carbon steel the larger the austenite grain size the larger will be the grain size of the transformation products on cooling, assuming all other conditions constant except the austenite grain size. An exception to this general rule is found in very pure iron such as electrolytic iron where small austenite grains may form very large ferrite grains on cooling through Ar_3.

6. In iron the larger the ferrite grain size, the larger will be the austenite grain size on heating above the Ac_3 transformation and vice versa.

7. The faster the rate of cooling of iron through the Ar-transformation range the smaller will be the ferrite grain and vice versa.

8. The faster the rate of heating of iron, other conditions remaining the same, the smaller will be the austenite grain size.

9. The greater the temperature gradient during the transformation on heating or cooling the larger will be the grain size.

10. If the grain size of a transformation product immediately after the transformation is smaller than the equilibrium grain size of that product under the existing conditions, the equilibrium grain size will be established by the known laws of grain growth.

11. A single grain when forced by thermal treatment to undergo a transformation must transform from at least one nucleus but may and nearly always does transform from more than one nucleus.

Doubt that there was any connection between the grain sizes of gamma and alpha iron or that the change of gamma iron to alpha or vice versa was in any way influenced by the previous state was expressed by Ruder in discussion of a paper by Jeffries.[390] Hoyt, in discussion of the same paper, also con-
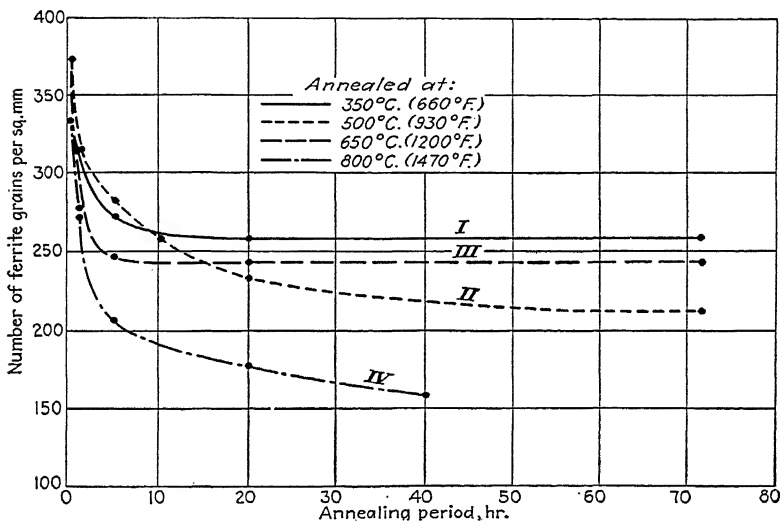
FIG. 104.—Grain growth in annealed Armco iron. (*Benson and Thompson.*[497])

cluded that grain inheritance would not be expected in pure iron or in alloys of iron and carbon containing less than 0.3 per cent carbon. On the other hand, Sauveur and Chou[3564] suggested that the martensitic structure in drastically quenched electrolytic iron was related to the arrangement of the crystallographic planes in gamma iron. This suggestion was substantiated by the work of Mehl and Smith.[1064]

The production of grain growth in basic open-hearth ingot iron, normalized at 950°C. (1740°F.) and annealed at temperatures between 350 and 800°C. (660 and 1470°F.) was reported by Benson and Thompson.[497] Their results (Fig. 104) showed

that there were distinct signs of grain growth after only 1 hr. at 350°C. (660°F.) but that the rate of growth fell off on prolonged heating, a stable condition being reached after 20 hr. At 800°C. (1470°F.) a very rapid increase in grain size occurred, the rate of growth falling off with prolonged heating, although still continuing after 40 hr. The results at 500°C. (930°F.) were similar to and intermediate between the 350 and the 800° curves, but results at 650°C. (1200°F.) were abnormal in that, up to 5 hours' annealing, the rate of growth was intermediate between the 500° and 800° rates, but from this point onward practically no further increase took place, the curve becoming intermediate between the 350° and 500° curves.

Five different methods can be used for determining the temperature of the commencement of recrystallization, according to Tammann and Salge:[741] (1) by the sudden increase in the angle at which two polished plates of metal, in contact, must be tilted to cause the upper plate to slide; (2) by the appearance on the polished surface of the metal of nodules which are visible under the microscope; (3) by the decrease in electric resistance; (4) by noting the temperature at which a stirrer will remain standing in a metal powder; and (5) by noting the temperature at which displacement of grain boundaries begins. For iron Tammann and Salge gave the following figures obtained by the above methods, presumably on different specimens of iron:

Method 1................................. 170°C. (340°F.)
Method 2................................. 220°C. (430°F.)
Method 3................................. 185°C. (365°F.)
Method 4................................. 148°C. (300°F.)
Method 5................................. 350°C. (660°F.)

Microscopic observation of electrolytic iron during heating and cooling was made by Rogers,[855,937] but no evidence of any marked change in crystal structure was found until the A_3 point was reached. A sample of cathode iron which had been carried part way through the A_3 transformation showed considerable grain growth in the portion which had been austenitic although that portion had been in the austenitic condition not more than 30 sec.

239. Summary of Data on Annealing.—Most of the effects of cold work in iron are removed by annealing at temperatures as low as 500°C. (930°F.) provided sufficient time is allowed.

For complete removal annealing at a temperature above 800°C. (1470°F.) is required. The temperature at which recrystallization begins in cold-worked iron decreases with increasing amount of deformation. With severe deformation recrystallization has been noted microscopically after annealing at temperatures as low as 350°C. (660°F.) but annealing at temperatures above 700°C. (1290°F.) is necessary to complete the recrystallization.

The annealing procedure necessary to remove the hardness of cathode electrolytic iron is similar to that for the removal of the effects of cold work. Longer annealing is necessary to attain minimum hardness than to attain complete recrystallization.

Annealing at temperatures above the A_3 point is necessary, according to most of the evidence, to cause recrystallization in iron not previously subjected to plastic deformation (excepting, of course, cathode iron). Whether the structure resulting from annealing is solely a function of the rate of cooling through the transformation or is influenced also by the structure of gamma iron is a subject of controversy. The information available is not sufficient to permit a conclusion on the factors which determine the structure of the metal after high-temperature annealing.

C. AGING

If the solid solubility of any of the constituents of a metal increases with increasing temperature, quenching from a high temperature may produce a condition of supersaturation at room temperature. Subsequent decomposition of the supersaturated solid solution during storage at moderate temperatures is accompanied by precipitation of the excess solute. This change affects the properties of the metal, the extent of the effect depending upon the amount and condition of agglomeration of the precipitate. The phenomenon has been termed "age hardening," "precipitation hardening," or more generally "aging." Our knowledge of the mechanism of aging is based to a considerable extent on data obtained on steel. However, the authors' review of the literature is confined to those investigations which reported data on high-purity or commercially pure iron; much material essential to a general treatment of the subject of aging is necessarily eliminated.

Although aging effects were noted in steels as early as 1873 by Caron[26] and in 1893 by Langley and Metcalf,[54] the earliest study of aging in iron seems to be that of Martens[89] who, in 1898, reported data showing its effect at room temperature on cold-worked ingot iron (Table 86). Aging in boiler plate was

TABLE 86.—INFLUENCE OF AGING ON THE TENSILE STRENGTH OF COLD-WORKED INGOT IRON*

Tensile strength before aging, lb. per sq. in.	Time of aging	Tensile strength after aging, lb. per sq. in.	Increase due to aging, lb. per sq. in.
78,070	30 min.	78,210	140
79,770	1 day	80,340	570
78,070	7 days	80,060	1990
77,500	30 days	84,750	7250
77,500	244 days	84,890	7390

* Martens.[89]

studied by Stromeyer[166,167,200] who concluded that the increase in brittleness upon aging was due to nitrogen or phosphorus or both.

240. Blue Brittleness.—The decrease in ductility of iron and steel in the blue-heat range 250 to 350°C. (380 to 660°F.) is commonly termed "blue-brittleness" and is now believed to be an aging effect. Most of the work on this subject prior to 1910 was reviewed by Robin,[220] and the more important investigations were reviewed in some detail by Fettweis.[398] From a study of his own data, as well as the data of previous investigators, Fettweis concluded that blue brittleness and aging are related phenomena, that in either case deformation initiates a process which results in increased strength and hardness and also in increased brittleness. With deformation and storage, both at ordinary temperatures, the increase in brittleness attains its maximum only after months or years, but increasing the temperature of storage accelerates the aging process until, in the blue-heat range, the embrittling process is completed in a fraction of a second. If the specimen is deformed at temperatures in the blue-heat range, the aging process requires only the same fraction of a second for its completion, thus producing the phenomenon termed blue brittleness. If the deformation occurs at tempera-

tures where recrystallization begins, above the blue-heat range, the embrittling process of deformation is counteracted by the softening process of recrystallization. If the rate of deformation
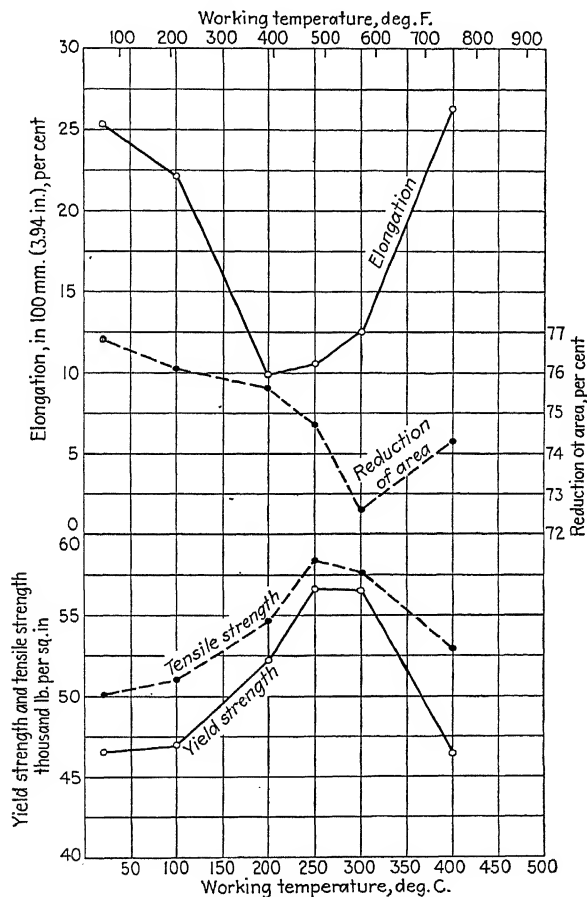
Fig. 105.—Effect of working temperature on the properties of ingot iron. (*Körber and Dreyer.*[(440)])

is slow as in the tensile test, there is sufficient time for the embrittlement to reach its maximum at a lower temperature than in the case where the rate of deformation is rapid, as in the

notched-bar impact test.   In the latter case a higher temperature
is necessary to accelerate the embrittling process to a correspond-
ingly rapid rate.   The subject was further investigated by
Körber and Dreyer[440] using ingot iron and steel.   One set of
specimens was deformed by stretching approximately 9 per cent
at temperatures between 20 and 400°C. (68 and 750°F.); a
second set was deformed about 9 per cent at room temperature
and aged at temperatures between 100 and 400°C. (210 and
750°F.); and a third set was stressed at room temperature and
aged at room temperature for various lengths of time.   Data for
the mechanical properties of the specimens of ingot iron used
by Körber and Dreyer are reproduced in Fig. 105 and Table 87.
Stressing ingot iron at 250 or 300°C. (480 or 570°F.) produced
maximum values for yield strength and tensile strength and
minimum values for elongation and reduction in area.   For ingot

TABLE 87.—EFFECT OF AGING ON COLD-WORKED INGOT IRON*

Stretching (at 20°C.), per cent	Temperature of aging		Time of aging	Yield strength,† lb. per sq. in.	Tensile strength, lb. per sq. in.	Elongation in 3.94 in., per cent	Reduction in area, per cent
	°C.	°F.					
8.7	20	70	1 hr.	46,500	50,100	25.3	76.5
8.3	20	70	45 days	50,600	52,500	23.7	76.6
8.3	100	210	1 hr.	50,600	52,600	21.8	75.6
9.2	200	390	1 hr.	51,000	53,900	20.2	76.4

* Körber and Dreyer.[440]
† For a permanent elongation of 0.025 per cent.

iron strained at room temperature, aging for 1 hr. at 200°C.
(390°F.) produced greater strength than did 1 hour's aging at
100°C. (210°F.).   The properties produced in strained ingot iron
as a result of aging for 1 hr. at 100°C. could be obtained by aging
at room temperature but 45 days were required.   From a
consideration of all their data, on specimens of steel as well as
of ingot iron, Körber and Dreyer concluded that specimens
strained at room temperature and then aged at elevated tempera-
tures never attained the brittleness of specimens strained at the
corresponding elevated temperatures.

Blue brittleness reaches its maximum in electrolytic iron in
the vicinity of 250°C. (480°F.), according to Sauveur and

Lee.[632] With carbon contents between 0.10 and 0.50 per cent the maximum strength of steel was reached in the vicinity of 325°C. (615°F.).   The presence of ferrite was necessary to obtain appreciable blue-heat phenomena.   The strength and hardness of normalized iron and steel were increased by stressing above the elastic limit, the increase becoming greater as the temperature of stressing was raised and being maximum after stressing in the blue-heat range.   Steels became softer when worked at temperatures above 580 to 680°C. (1075 to 1255°F.), but electrolytic iron hardened upon stress at any temperature below the critical. Sauveur[904] found that the blue-heat phenomena in basic open-
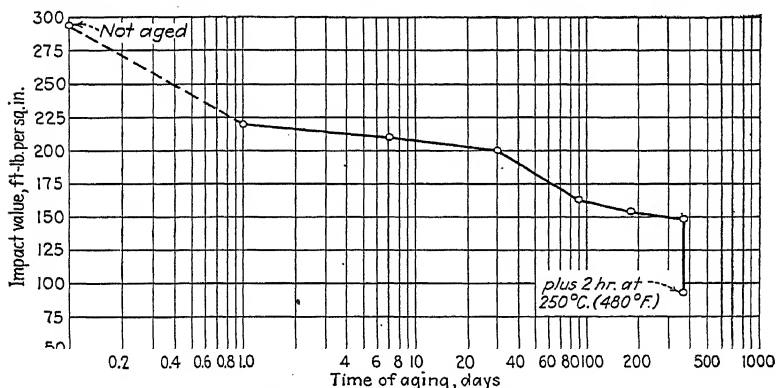
Fig. 106.—Effect of time of aging on impact values of compressed bars of ingot iron.   (*Bauer.*[427])

hearth ingot iron, as revealed by torsion tests, increased to a maximum at 300°C. (570°F.), further increase in temperature resulting in a marked decrease in strength and stiffness.

241. Effect of Time and Temperature of Aging on the Properties of Iron.—The brittleness of specimens of ingot iron, reduced in thickness by compression and aged at room temperature, increased more rapidly during the early stages of aging than during the later stages, according to the data of Bauer[427] shown in Fig. 106.   That aging at room temperature for 360 days was not sufficient to complete the process was indicated by the increase in brittleness of an aged specimen as a result of tempering at 250°C. (480°F.) for 2 hr.   The brittleness of the specimens was measured by the notched-bar impact test.

TABLE 88.—EFFECT OF PRIOR DEFORMATION AND TEMPERATURE OF AGING ON THE YIELD STRENGTH OF ELECTROLYTIC IRON*

Aged 30 min. at		Yield strength† after aging, lb. per sq. in., for prior deformation of			Maximum stress, lb. per sq. in., used to produce deformation before aging of		
°C.	°F.	1%	5%	20%	1%	5%	20%
50	120	17,100	27,000	......	13,400	23,500	
100	210	19,600	29,700	37,400	13,200	23,500	31,900
300	570	15,600	27,400	37,700	13,100	23,500	33,300
500	930	13,500	19,900	26,600	12,800	23,000	32,000

* Ludwik and Scheu.[620]
† Reported as Streckgrenze: from stress-strain diagram.
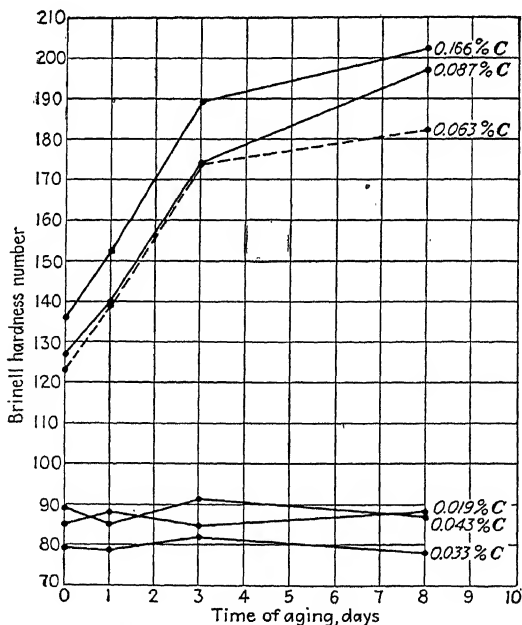
FIG. 107.—Effect of aging, at room temperature, on the hardness of quenched iron-carbon alloys. (*Masing and Koch.*[730])

As a result of work with Heraeus electrolytic iron Ludwik and Scheu[620] found that aging for 3 months at 20°C. (68°F.) or for 1 hr. at 100°C. (210°F.) increased the tensile strength and restored the break in the stress-strain curve of specimens previously quenched from 500°C. (930°F.). Ludwik and Scheu also aged, at 20°C. and for various lengths of time, electrolytic iron which had previously been stretched 1 per cent. The yield strength increased progressively with increased duration of aging from 15,000 lb. per sq. in. for a specimen aged for 30 min. to 18,000 lb. per sq. in. after 3 months' aging. Aging electrolytic iron for 30 min. at 50, 100, 300, and 500°C. (120, 210, 570, and 930°F.) after prior elongations of 1, 5, and 20 per cent, as shown in Table 88, increased the yield strength to higher values than the maximum stress in the preliminary plastic deformations in all cases except that of iron aged at 500°C. (930°F.) after 5 or 20 per cent prior deformation. The changes in yield strength of electrolytic iron and ingot iron during aging and at "blue heat" were ascribed by Ludwik[675] to changes in the solubility of minor constituents in the metal just as in the case of aluminum alloys.

Aging effects as measured by Brinell hardness in a series of iron-carbon alloys prepared from electrolytic iron were studied by Masing and Koch.[730] After quenching from 700°C. (1290°F.), specimens with over 0.043 per cent carbon showed considerable increase in hardness upon aging, but specimens with lower carbon contents showed only a slight increase. Their data are shown in Table 89 and Fig. 107.

242. Rôle of Nitrogen and of Oxygen in Aging.—The rôle of nitrogen in the aging or dispersion hardening of iron was investigated by Dean, Day, and Gregg.[818] Three kinds of iron were used: (1) vacuum-melted electrolytic iron, (2) electrolytic iron melted in air, and (3) basic open-hearth ingot iron. These materials were annealed at 980°C. (1795°F.) in vacuum, reduced 30 per cent in thickness by cold rolling, and then reheated to temperatures from 100 to 500°C. (210 to 930°F.). The vacuum-melted electrolytic iron showed no increase in hardness after aging, the air-melted iron increased markedly in hardness after aging at 250°C. (480°F.), while the basic open-hearth ingot iron was intermediate. Treatment with ammonia gave the vacuum-melted electrolytic iron age-hardening properties similar to those of the air-melted iron. Nitriding the ingot iron increased the

TABLE 89.—BRINELL HARDNESS OF AGED IRON-CARBON ALLOYS, PREVIOUSLY
ANNEALED 1 HR. AT 700°C. AND QUENCHED*

No.	Composition, per cent			Brinell hardness			
				Immediately after quenching	Aged		
	C	Si	P		1 day	3 days	8 days
Aged at room temperature
1	0.019	......	.....	85	88	84.5	88
5†	0.033	0.0065	0.031	79	78.5	82	78
6	0.043	......	.....	89	85	91	87
7	0.087	......	.....	127	140	174	197
8	0.166	......	.....	136	152	199	202
9†	0.063	0.0087	0.023	123	139	174	182
Aged at 50°C. (120°F.)
1	0.019	......	.....	85	85	85	92
5†	0.033	0.0065	0.031	79	80	82	80
6	0.043	......	.....	89	96	103	101
7	0.087	......	.....	127	168	175	170
8	0.166	......	.....	136	201	197	194
9†	0.063	0.0087	0.023	123	194	210	207

* Masing and Koch.[730]
† Sulphur less than 0.001 per cent.

brittleness in the 200 to 300°C. (390 to 570°F.) range, while
annealing the ingot iron for 12 hr. at 1100°C. (2010°F.) in
hydrogen eliminated the temper brittleness. The tensile
strength of the nitrided ingot iron containing 0.086 per cent
nitrogen, after quenching from 500°C. (930°F.), was about
64,000 lb. per sq. in. After aging for 50 hr. at room temperature
this was increased to about 88,000 lb. per sq. in., accompanied
by a decrease in elongation and reduction in area. It was
concluded that commercial irons owe their property of hardening,
by reheating after cold work, as well as their increase in tensile
strength in the range 100 to 300°C. (210 to 570°F.), to the solution
of small amounts of iron nitride and that the iron-nitrogen
system is a dispersion hardening system in which a marked
degree of hardening can occur at room temperature.

The effect of oxygen and nitrogen upon the aging of iron was investigated by Eilender and Wasmuht[821] using ingots prepared from basic open-hearth ingot iron. Their conclusion, based on the results shown in Table 90 and in Fig. 108, was that the oxygen content of iron, except at a critical value of about 0.06 per cent, had no material influence upon precipitation hardening after
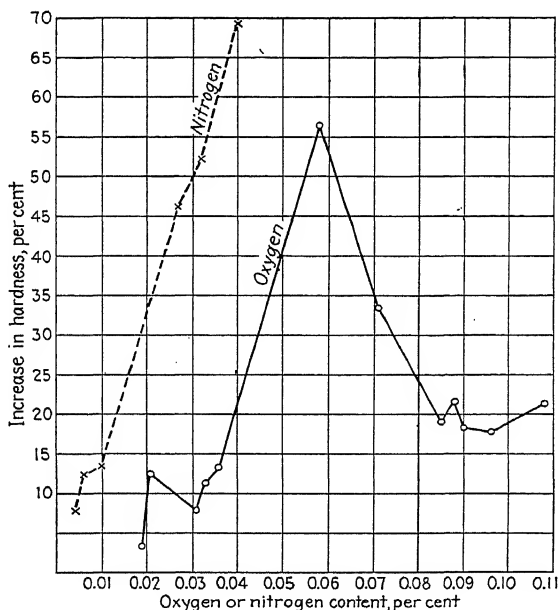
FIG. 108.—Variations of hardness with oxygen or nitrogen content in quenched and aged iron. (*Eilender and Wasmuht.*[821])

quenching from 680°C. (1255°F.). They stated that, if the oxygen present was combined with silicon or aluminum, it had no effect upon precipitation hardening; only oxygen present as ferrous oxide or manganous oxide was effective in that respect. According to the recent results of Burns,[1048] carbon and nitrogen are effective in developing precipitation hardening of iron, but oxygen does not play a significant part in the process.

In Eilender and Wasmuht's experiments, the specimens with varying nitrogen contents also were quenched from 680°C.

TABLE 90.—EFFECT OF OXYGEN ON THE CHANGE IN HARDNESS OF IRON
AFTER QUENCHING AND AGING*

Sample	Composition, per cent			Brinell hardness				
	C	N	O	Normal-ized	Quenched from 680°C. (1255°F.)	Aged 14 days at room temperature	In-crease, actual	In-crease, per cent
1	0.011	0.005	0.019	88.4	91.0	94	3.0	3.3
2	0.011	0.006	0.021	82.4	92.4	104	11.6	12.5
3	0.010	0.004	0.031	89.5	85.1	91.7	6.6	7.8
4	0.009	0.005	0.033	81.7	79.7	88.8	9.1	11.4
5	0.012	0.010	0.036	100.1	108.7	123.3	14.6	13.4
6	0.014	0.003	0.058	81.7	101.0	158.0	57.0	56.5
7	0.017	0.005	0.071	83.1	101.9	136	34.1	33.5
8	0.013	0.010	0.085	87.2	94.1	112	17.9	19.0
9	0.014	0.007	0.088	81	101.9	124	22.1	21.7
10	0.012	0.001	0.090	97.1	94.7	112	17.3	18.3
11	0.012	0.006	0.096	88.7	91.7	108	16.3	17.8
12	0.011	0.009	0.108	79.1	87.3	106	18.7	21.4

* Eilender and Wasmuht.[821]

TABLE 91.—EFFECT OF NITROGEN ON THE CHANGE IN HARDNESS OF IRON
AFTER QUENCHING AND AGING*

Sample	Composition, per cent			Brinell hardness				
	C	N	O	Normal-ized	Quenched from 680°C. (1255°F.)	Aged at room temperature†	In-crease, actual	In-crease, per cent
a	0.010	0.004	0.031	89.5	85.1	91.7	6.6	7.8
b	0.011	0.006	0.021	82.4	92.4	104.0	11.6	12.5
c	0.012	0.010	0.031	100.1	108.7	123.3	14.6	13.4
d	0.010	0.027	0.074	93.2	110.8	162.0	51.2	46.3
e	0.015	0.032	0.046	104.7	118.2	180.0	61.8	52.2
f	0.013	0.040	0.046	102.8	120.4	204.0	83.6	69.4

* Eilender and Wasmuht.[821]
† Duration of aging not stated; presumably it was 14 days. See Table 90.

(1255°F.) and aged at room temperature. The duration of the aging treatment was not stated but presumably was the same as for the series of specimens which contained oxygen. The
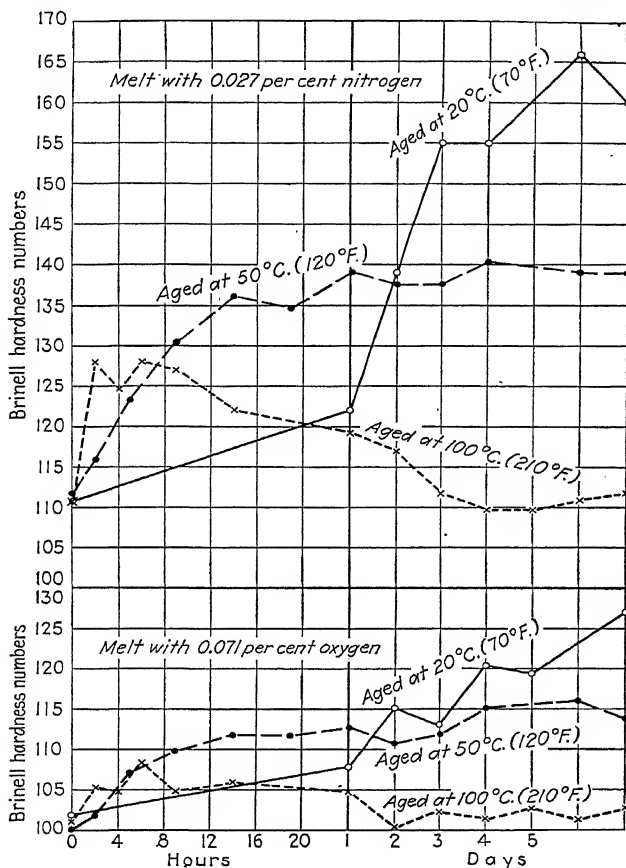
FIG. 109.—Effect of time and temperature of aging on the hardness of oxygen-containing and nitrogen-containing irons. (*Eilender and Wasmuht.*[821])

slight precipitation hardening which occurred with nitrogen contents of 0.01 per cent or less, as shown in Table 91 and Fig. 108, was ascribed to the carbon. With nitrogen contents of 0.027 per cent or more there was a rapid increase in hardness which reached

a maximum after a few days of aging. The data on the effect of nitrogen are open to the criticism that the specimens which showed the effect of aging were high in nitrogen but also were high in oxygen; the amounts of oxygen present in these age-hardening alloys approached the "critical amount" (0.06 per cent) which produced age hardening in the specimens which contained oxygen alone. The variations in age hardening in the nitrogen specimens may be due, in part at least, to differences in oxygen content. Investigation of the effect of aging temperature, as shown in Fig. 109, indicated that aging at room temperature produced maximum hardness but only after a relatively long time. With increasing aging temperature the maximum hardness attained was lower but the time necessary to reach this maximum was much shorter.

243. Conditions Necessary for Aging.—Eilender and Wasmuht[321] stated that the conditions under which precipitation hardening may take place are as follows:

1. The solubility of the substance contained in solid solution in the base metal must decrease with decreasing temperature.

2. The amount of the substance absorbed in solid solution at higher temperatures must be retained in solution after quenching, that is, the alloy must be capable of undercooling.

3. On aging at room temperature or slightly above an amount of the substance corresponding to equilibrium conditions must be slowly precipitated out of solution in highly dispersed form.

244. Aging of Nitrided Electrolytic Iron.—Köster[337] studied the effect of quenching and tempering on the mechanical properties of nitrided electrolytic iron and steel. His specimens of electrolytic iron were nitrided for 6 hr. in ammonia at 550°C. (1020°F.) to produce a case 0.5 mm. thick with an average nitrogen content of 0.12 per cent. The nitrided specimens were cooled at different rates from the nitriding temperature, and the effect of this treatment and of subsequent tempering or aging, on the mechanical properties, was determined. The results obtained for electrolytic iron are shown in Table 92. Specimens quenched from 550°C. (1020°F.) showed considerably increased strength but had completely lost their ductility and broke without necking down. Tempering the quenched material at 250°C. (480°F.), for 1 hr., restored the ductility. Specimens slowly cooled from 550°C. were only slightly stronger and were approxi-

TABLE 92.—MECHANICAL PROPERTIES OF NITRIDED ELECTROLYTIC IRON
AFTER QUENCHING AND TEMPERING*

Treatment	Yield strength,† lb. per sq. in.	Tensile strength, lb. per sq. in.	Elongation, $l = 11.3\sqrt{A}$, per cent	Reduction in area, per cent
Not nitrided..............	22,000	38,000	48	87
Nitrided at 550°C. (1020°F.) and cooled slowly.......	23,000	40,500	35	81
Quenched from 550°C. after nitriding...............	28,500	45,000		
Quenched from 550°C., then tempered at 250°C. (480°F.)...............	24,500	45,500	30	80

* Köster.[837]
† Reported as Streckgrenze.

mately equal in ductility, as compared to the original material.
The Brinell hardness of the original electrolytic iron was about
100; that of the nitrided and quenched material was about 190;
aging at room temperature for 28 days increased the Brinell
hardness of this material to about 240. Köster interpreted these
results as showing that nitrogen, in these amounts, exists in solid
solution in alpha iron at 550°C. (1020°F.) and exists in a super-
saturated solid solution if the material is quenched from 550°C.
The quenched material is susceptible to aging at room tempera-
ture and hardens in a manner similar to that of duralumin. If
the nitrogen is precipitated from the supersaturated solution by
means of tempering treatments, the working properties may be
restored. The only tempering treatment applied to electrolytic
iron to restore the working properties was at 250°C. (480°F.),
but in additional work with steel specimens it was found that
tempering for 1 hr. at 150°C. (300°F.) was sufficient to effect the
precipitation of nitrogen and to restore the working properties.
The conclusions were substantiated by microscopic observations.

245. Miscellaneous Data on Aging.—In another investiga-
tion[838] Köster found that electrolytic iron containing 0.01 per
cent carbon showed no age hardening, basic open-hearth iron
only slight age hardening, and Swedish iron rather strong age
hardening, as indicated by the increase in coercive force.
Bates,[917] however, in a reply to discussion of his paper reported

that electrolytic iron containing 0.02 per cent carbon showed marked age hardening after a quench from 700°C. (1290°F.). Basic open-hearth ingot iron showed only a slight age hardening after quenching from 700°C. but considerable after quenching from 900°C. (1650°F.).

As a method of studying the age hardening of iron and steel, Sauveur and Burns[1026] proposed the use of the Brinell impression as a means of cold working, the hardness of the metal at the bottom of the depression being measured by the Rockwell test. Results obtained by this method on annealed basic open-hearth ingot iron were:

Rockwell *B* hardness, not aged......................	76.8
Rockwell *B* hardness, aged 1 hr. at 100°C. (210°F.).....	86.5
Increase, per cent................................	12.6
Rockwell *B* hardness, not aged......................	80.9
Rockwell *B* hardness, aged 30 days at room temperature	88.0
Increase, per cent................................	8.8

Ehn[923] discussed the age hardening of iron and steel and the rôles of carbon, nitrogen, copper, tungsten, and beryllium in that phenomenon as follows: When iron or steel is cooled slowly from 650 to 750°C. (1200 to 1380°F.), carbon present in excess of 0.01 per cent precipitates and the resulting carbide migrates to the grain boundaries. If the steel is quenched from 650 to 750°C. the carbon remains temporarily in unstable solid solution and gradually precipitates in highly dispersed particles within the matrix of the alpha-iron crystals. These particles of cementite form keys which prevent movement along the slip planes, thus hardening the metal. Tempering at 50 to 100°C. (120 to 210°F.) speeds up the precipitation and, therefore, the age hardening but with higher tempering temperatures there is a tendency for the precipitated particles to agglomerate with less hardening effect.

According to Ehn, nitrogen is soluble in alpha iron at room temperature to the extent of about 0.01 per cent, but its solubility increases much more rapidly with increasing temperature, about 0.5 per cent being soluble in alpha iron at 580°C. (1075°F.). After iron or steel containing nitrogen is quenched, the nitrogen

in solution precipitates in time as thin plates of nitrides. These plates are much more difficult to coalesce than are the cementite particles, hence precipitation hardening by nitrogen can be effected at much higher tempering temperatures than is the case when carbon is the active agent.

As a copper content considerably above 0.4 per cent is necessary to cause precipitation hardening, this element is not a factor in the aging of high-purity iron or commercially pure iron. The same is true of tungsten and beryllium as precipitation hardening agents.

An excellent discussion of the data and theories of age hardening, precipitation hardening, and blue brittleness in iron and steel was presented by Mehl.[897]

246. Summary of Data on Aging of Iron.—The phenomenon of aging in metals results from the formation, as a result of rapid cooling from elevated temperatures, and the subsequent decomposition at moderate temperatures, of supersaturated solutions in which certain impurities or minor constituents are present in amounts in excess of the solid solubility at room temperature. Aging may occur in iron if carbon or nitrogen is present in excess of their respective limits of solid solubility at room temperature; oxygen probably does not play a significant part. The hardness resulting from aging of iron can be removed by annealing at temperatures above 200°C. (390°F.), presumably through agglomeration of the precipitated phase. Aging has not been encountered in vacuum-melted electrolytic iron.

D. AUTHORS' SUMMARY

The hardening of steel or of irons of commercial purity, due to quenching as ordinarily practiced in heat treatment, results from the presence of another element, usually carbon. Consequently, high-purity iron would not be expected to exhibit quench hardening, although there is some evidence that it may be hardened by unusually severe quenching, *i.e.*, by cooling at an extremely rapid rate from a very high temperature.

Annealing can be employed to remove strains and to increase the grain size of-iron. The degree of removal of these effects depends upon both the time and temperature of the annealing treatment. Most of the effects of cold work can be removed by an extended anneal at 500°C. (930°F.), but complete elimination

is obtained only by annealing at a temperature above 800°C. (1470°F.). The tendency of cold-worked iron to recrystallize increases with increasing amounts of deformation. After severe deformation the beginning of recrystallization has been observed at temperatures as low as 350°C. (660°F.), but annealing at 700°C. (1290°F.) or higher is necessary to complete the recrystallization. In iron which has not been previously strained, annealing at temperatures above the A_3 point is necessary to cause recrystallization.

Age hardening, like quench hardening, results from the presence of impurities or minor constituents in a metal. Consequently it would not be expected to occur in high-purity irons and it has not been encountered in vacuum-melted electrolytic iron. Aging may result from the presence of carbon or nitrogen in iron; the ensuing hardness can be removed by annealing at temperatures above 200°C. (390°F.).

CHAPTER XII

EFFECT OF MINOR CONSTITUENTS

Aluminum to Copper—Gold to Nickel—Nitrogen and Oxygen—
Phosphorus to Zinc—Miscellaneous Constituents—Authors' Summary

Any discussion of the effect produced by the presence of foreign substances in iron should be based upon the knowledge of the physical condition in which the substance exists in the metal. Smithells[907] ably discussed the advisability of using the designation "minor constituents" rather than "impurities" in referring to such foreign substances in a metal. An arbitrary numerical limit cannot be established which will be equally applicable to all minor constituents, but for each particular substance the iron-rich alloys of that particular series should be considered. Although this may extend the discussion somewhat beyond the limit of "impurities," this is often necessary in order to establish the trend of the resulting effects. This chapter becomes, then, essentially a metallographic discussion of the iron-rich alloys of the various binary iron-alloy systems.

Because of the preponderant influence of the transformations of iron upon its properties, special attention has been given to this. Also, since change in mechanical properties by aging, either incidental or intentional, is dependent upon the limit of solid solubility of some foreign substance in the parent metal together with the change in this limit with change in temperature, these factors are important. Likewise, if the foreign substance exists in solid solution, the manner in which it is built into the crystal lattice of the parent metal is of importance. Information of this kind is often meager and fragmentary.

In the ensuing discussion the various minor constituents are considered in alphabetical order.

A. ALUMINUM TO COPPER

247. Aluminum.—Aluminum enters readily into solid solution in iron. According to the recent work of Osawa,[1021] the limit of

solubility is 32 per cent, which does not differ greatly from the value of approximately 33 per cent reported years ago by Gwyer.[178]   The solubility limit remains unchanged with rising temperature up to approximately 900°C.   It has been shown by Wever and Müller[370] as well as by Osawa[1021] that the presence of a small amount of aluminum in iron raised the temperature of the A_3 transformation and lowered A_4, the result being a "loop" in the equilibrium diagram, inclosing the gamma-iron field.   The maximum width of the loop corresponded to about 1 per cent aluminum according to Wever, whereas Iwase (cited by Wever) placed it at 1.2 per cent.   The effect of aluminum on the A_2 transformation has been shown by Osawa[1021] to consist in lowering the transformation so that with an aluminum content of 15 per cent it occurs below room temperature.

The introduction of aluminum into alpha iron results in an increase in the parameter of the body-centered cubic lattice, the change with progressively increasing amounts of aluminum being practically a linear one.   The value given by Osawa for the solid solution containing 10 per cent aluminum, $a = 2.877$ Å., was somewhat less than the value 2.890 ± 0.005 Å. which was reported by Wever[370] for the alloy containing 11.6 per cent aluminum.   The density calculated on the basis of the latter value agreed closely with the observed density, according to Wever.   It was found to decrease linearly with the increase of aluminum content from 7.88 g. per cu. cm., the value given for pure iron, to 6.78 g. per cu. cm. for iron containing 11.6 per cent aluminum.   The values obtained by Bradley and Jay[962] agreed with those of Wever.   According to these investigators, the linear relationship in the increase in lattice parameter with increasing aluminum content does not extend beyond the solid solution containing approximately 10 per cent aluminum. Aluminum may also exist in iron as the oxide, and advantage is taken of this fact in the preparation of certain iron catalysts.[977] The activation of some catalysts prepared by the reduction of pure iron oxide is greatly influenced by the presence of aluminum. Apparently this is an effect depending on grain size, the aluminum oxide disseminated through the iron being an excellent obstructant to grain growth.

248. Antimony.—Antimony forms a eutectiferous series with iron.[181]   At approximately 1000°C., iron can hold 5 per cent

antimony in solid solution. Aside from this, information on iron containing small amounts of antimony is lacking.

249. Arsenic.—Arsenic, in small amounts in iron, exists as a solid solution. Aside from the fact that at the eutectic temperature, 827°C., arsenic is soluble in iron to the extent of approximately 6.8 per cent,[156,527] the limits of solid solubility have not been determined. Likewise, little is known concerning the effect of arsenic on the transformations in iron. According to Oberhoffer and Gallaschik,[527] the solid solution exists as delta iron above 1440°C. The presence of arsenic appears to produce a marked hysteresis in the A_2 transformation. The temperature of this transformation in iron containing 0.5 per cent arsenic, as determined by a heating curve, appears to be unchanged. On a cooling curve, however, the transformation temperature appears to be lowered by approximately 80°C.

250. Beryllium.—According to Oesterheld,[353] beryllium is soluble in iron to the extent of 6.4 per cent at 1160°C. and 4.9 per cent at 650°C. The limit of solid solubility at room temperature has not been accurately determined. However, the results obtained by Kroll[840] on the age hardening of iron containing beryllium show that this limit lies between 1.2 and 3 per cent. Iron containing the smaller amount of beryllium showed only slight increase in hardness upon reheating after quenching, whereas in iron containing 3 per cent beryllium an increase of more than 50 per cent in the Brinell hardness resulted from the same treatment. The results of Seljesater and Rogers[982] served to place the solid-solubility limit somewhat more accurately. These investigators observed a marked increase in hardness in iron containing 2.8 per cent beryllium and a slight increase with 1.4 per cent. Wever and Müller[870] established the fact that the solubility of beryllium in gamma iron is very limited and that its presence results in a closed gamma field. The temperature of the A_4 transformation was found to be lowered by beryllium and that of A_3 to be raised; the maximum extent of the closed gamma field thus formed corresponded to 0.5 per cent beryllium at approximately 1050°C. All solid solutions of beryllium in iron other than those corresponding to the closed gamma field between the temperatures of the A_3 and A_4 transformations have a body-centered lattice, in other words, there is no distinction other than that of temperature

between the delta or high-temperature stable form and the alpha or low-temperature form of iron-beryllium solid solution.

Wever and Müller have shown, by the comparison of observed and computed densities, that the solid solution of beryllium in iron is of the atom-substitution type and a slight decrease in the parameter of the body-centered cubic lattice results from the addition of beryllium to iron. A value of $2.83_8 \times 10^{-8} \pm 0.003$ cm. was found for the lattice parameter of the solid solution containing 1.23 per cent beryllium.

The A_2 transformation in iron was found by Wever and Müller to be lowered slightly by the addition of beryllium. A temperature of 700°C. was found for the solid solution containing 1 per cent beryllium, the lowering of the temperature with respect to the beryllium content being a linear relationship.

251. Boron.—The solubility of boron in iron is very limited at all temperatures. According to Wever and Müller,[870] who have studied this system extensively, the maximum solubility of boron in each of the forms of iron, alpha, gamma, and delta, is 0.15 per cent. These investigators concluded, partly on theoretical reasoning, that the temperature of the A_4 transformation was lowered by boron to 1381°C. and that of A_3 was raised to 915°C. Although boron was classed by them with the other elements which produce a closed gamma field, the case is not strictly analogous since the alpha and delta fields are not continuous. The solubility in gamma iron was stated by them to range from 0.10 per cent at 1380°C. to 0.15 per cent (the maximum) at 1174°C., the eutectic temperature. At all temperatures below this, iron containing more than 0.15 per cent boron showed in its microstructure a second phase, the compound Fe_2B. The temperature of A_2 was not affected by the presence of boron, and its solubility in alpha iron below this transformation has not been determined. However, it is apparently extremely small.

252. Cadmium.—Cadmium is not a common impurity in iron and very little is known concerning its influence. It forms alloys with iron as is indicated by the well-known fact that it can be used for coating iron by the hot-dipping process.[793] The negative results of the early work of Isaac and Tammann[158] in attempting to alloy the two metals are undoubtedly responsible for the classification of cadmium as a metal which is insoluble in iron.[810]

253. Carbon.—Of the three transformations in iron the temperature of only one, the A_3 or alpha-gamma change, is affected in a significant manner by the presence of small amounts of carbon. As is well known, the temperature of this transformation is continuously lowered by progressively increasing amounts of carbon up to the eutectoid composition. This point and the effect of carbon on the properties of iron are discussed in detail in another monograph of this series,* "The Alloys of Iron and Carbon."

The difference in the solubility of carbon in the alpha or body-centered-lattice form of iron and the gamma or face-centered-lattice form is very great and this fact, of course, is fundamental in the heat treatment of steels. The limit of solubility of carbon in alpha iron, or ferrite, is still in doubt. The situation has not changed since 1929 when the subject was critically reviewed by Gillett.[829] The value 0.035 per cent, based on the data given by Scott,[489] for the maximum solubility at the temperature of the A_1 or eutectoid transformation seems the most probable one, although there is evidence to indicate that the presence simultaneously of other impurities in the iron may affect this value to some extent. According to Grossmann[832] dissolved oxygen, apart from the precipitated oxide particles, favors an increase in the solubility of carbon in alpha iron. The limit of solubility of carbon at room temperature is, as yet, not fully determined. That it is less than the value given above is evident from the results obtained by Whiteley[751] and by Masing and Koch,[730] who showed that low-carbon iron will respond to a precipitation-hardening treatment, that is, quenching followed by reheating below the alpha-gamma transformation. An approximate value of 0.01 per cent, based upon the work of Yensen,[871] is accepted by many. The solid solution of carbon in iron is generally believed to be of the interstitial type rather than the substitutional, which is true for the solutions of most other elements in iron.

Esser and Müller[997] measured the lattice parameter of iron-carbon alloys at temperatures up to 1100°C. Representative results are summarized in Table 93. In addition to the progres-

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* To be published soon.

Table 93.—Lattice Parameter of Iron-carbon Alloys at Different Temperatures*

Carbon, per cent	Parameter (800°C.), Å.	Parameter (1100°C.), Å.	Increase	
			Å.	Per cent
0.1	3.6427	3.6606	0.0179	0.49
0.33	3.6446	3.6651	0.0205	0.56
0.57	3.6494	3.6742	0.0248	0.68
0.82	3.6589	3.6886	0.0297	0.81
1.16	3.6648	3.6973	0.0325	0.88
1.52	3.6634	3.7011	0.0377	1.02

* Esser and Müller.[997]

sive increase with increasing carbon content, the results show that the increase in the parameter with temperature, from 800 to 1100°C., is dependent upon the carbon content, the percentage increase for the high-carbon steel being essentially twice that of the steel of very low carbon content.

254. Cerium.—Such knowledge as is available on the effect of cerium on iron[385] indicates a solid solubility in gamma iron to the extent of 15 per cent at 1090°C. and 10 per cent at 900°C. Twelve per cent has been given as the limit of solubility in alpha iron, and information on the change of solubility with temperature is lacking. The temperature of the A_2 transformation appears to increase slightly with increasing cerium content. It occurs at 800°C. in the alloy containing 10 per cent.

255. Chromium.*—The generally accepted statement[705,804] that iron and chromium form a continuous series of solid solutions should be slightly modified in view of the discovery by Bain[649] that the solubility of chromium in gamma iron is limited. By means of microstructural studies and X-ray examination, Bain showed that approximately only 14 per cent is soluble in gamma iron. The same discovery was made independently by Oberhoffer and Esser[734] by means of thermal analysis and X-ray examination. They concluded that the temperature of the A_4 transformation was lowered about 26°C. for the addition of

* For a complete discussion of the effect of chromium in iron the reader is referred to another monograph in this series, "The Alloys of Iron and Chromium," now in preparation.

each per cent of chromium. The temperature of the A_3 transformation was stated to be lowered to approximately 820°C. by the addition of 8 per cent chromium, but with further additions it was raised to 900°C. Kinzel[788] confirmed the general findings of the other investigators and set the limit of solubility of chromium in gamma iron as 12.2 per cent. His dilatation measurements showed the marked drop in the temperature of the A_4 transformation with increasing chromium content but showed no appreciable change in the temperature of the A_3 transformation.

The A_2 transformation is not greatly changed by the presence in iron of small amounts of chromium. According to Oberhoffer and Esser,[734] a small addition of chromium results in a slight rise of the temperature of the A_2 transformation, but with further addition the temperature is lowered so that in an alloy containing approximately 7 per cent the A_2 temperature is about the same as for iron containing no chromium.

256. Cobalt.—Cobalt enters into solid solution in iron in all proportions. There appears to be no uncertainty concerning the constitution of the alloys of low cobalt content. In these alloys the temperature of each of the transformations in iron is raised continuously by progressively increasing amounts of cobalt.[292,676] The A_4 transformation is raised to 1490°C. by 15 per cent cobalt, the maximum amount soluble in delta iron. Both the A_3 and A_2 transformations occur at approximately the same temperature, 920°C., in the same alloy. The solid solution of cobalt in iron is of the atom-substitution type and, with an increasing cobalt content up to 80 per cent,[424] the body-centered lattice is maintained as the only phase. The results obtained by Honda[402] and by Schulze[740] on the changes in the physical properties of these alloys with increasing cobalt content are in good agreement with the observed crystal structure only for the solid solutions of low cobalt content.

257. Copper.—Available data on the alloys of iron and copper have been reviewed in another monograph of this series,[1055] and in a résumé on the constitution of iron-copper alloys by Gregg and Daniloff.[1001] The effect of copper in small amounts on iron is very similar to the corresponding effect of carbon. Iron dissolves copper to a limited extent, the limit of solid solubility depending upon the temperature.

The limit of solid solution of copper in iron at room temperature has not been definitely determined; however, it appears to be only slightly less than at 600°C. where it is 0.4 per cent. With increasing temperature, from 600 to 810°C., it increases from 0.4 to 3.4 per cent. The temperature 810°C. is the eutectoid horizontal corresponding to the pearlite line in the iron-carbon diagram. It follows, therefore, that the A_3-transformation temperature is affected by the presence of copper, being lowered to 810°C. by 3.4 per cent copper.* The A_2 transformation is only slightly affected by the presence of copper, 759°C. being reported by Ruer and his coworkers. The limit of solubility of copper in gamma iron is greater than that for alpha iron, being nearly 10 per cent in the neighborhood of 1400°C. The gamma-delta transformation is of the nature of a peritectoid reaction occurring at 1477°C.

At all temperatures below the eutectoid horizontal (810°C.), the iron-copper alloy system consists of only two phases, one of these being the saturated solid solution of copper in iron, the other the corresponding solution of iron in copper. In iron containing copper somewhat in excess of the solid-solution limit at room temperature, a second phase will be detected in the microstructure. Since the solid-solution limit of copper in iron varies with temperature, it follows that the amount of the second phase in alloys having a copper content only slightly in excess of the solubility limit can be varied at will within rather wide limits by treating the alloy in a suitable manner. A practical application can be made of this fact, the mechanical and other properties of the metal being varied correspondingly (see aging, p. 431, and also "The Alloys of Iron and Copper"[1055]).

B. GOLD TO NICKEL

258. Gold.—The early work of Isaac and Tammann[160] still stands as the main source of information on iron-gold alloys. The limit of solid solubility of gold in alpha iron is approximately 18 per cent. The change of this limit with temperature has not

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* As a result of recent X-ray studies of electrolytic iron, Norton[1066] concluded that the maximum solubility of copper in iron is about 1.4 per cent by weight at the eutectoid temperature of 850°C. and that the solubility is constant, at 0.35 per cent copper, at all temperatures below approximately 650°C.

been determined. Jette and his associates[1057] in a recent X-ray study have determined the parameter of the body-centered cubic lattice of iron containing 2 per cent gold to be 2.8643 Å., an increase of 0.094 per cent over the parameter of iron. The temperature of the A_2 transformation in iron is apparently unaffected by the presence of gold.

259. Hydrogen.—Hydrogen occurs more frequently as an impurity in iron than is commonly supposed. It has been known since the early work (1863) of St. Claire-Deville and Troost that hot iron is readily permeated by hydrogen. According to the extensive studies of Sieverts and his associates,[859] and to results obtained by Martin[844] on electrolytic iron, hydrogen is absorbed by iron at temperatures of 400 to 500°C., the solubility increasing linearly with increasing temperature up to the A_3 temperature. The change of the iron to the gamma form is accompanied by a sudden increase in the solubility of the hydrogen and, with increasing temperature up to the melting point, the solubility increases linearly at a slightly greater rate than in alpha iron. Data recently published by Luckemeyer and Schenck[1017] are in good agreement with the results of Sieverts and of Martin. Electrolytic iron, open-hearth iron, and carbonyl iron were the materials used. These investigators also reported a sudden decrease in the solubility of hydrogen in iron as the metal changes at the A_4 transformation from the face-centered cubic lattice of gamma to the body-centered lattice of delta iron. On the other hand, the results obtained by Iwase[672] on iron reduced from the oxide, although showing a marked difference in the rate of solution in the alpha and gamma forms of iron, did not confirm the sudden change in solubility as the iron changed from one allotropic form to another. Iwase found the solubility of hydrogen in both forms to be considerably higher than was reported by Sieverts and by Martin, also the difference between the solubility rates in the two forms to be much greater, as is shown in Table 94.

Hydrogen in the atomic state is readily absorbed by alpha iron at room temperature,[412] and electrolytic iron as well as iron which has been "over pickled" in acid usually contains considerable hydrogen. According to Davey[656] the "tunnels" or interatomic spaces in the iron crystals are large enough to permit the movement of hydrogen atoms but not of hydrogen

TABLE 94.—SOLUBILITY OF HYDROGEN IN IRON AT ATMOSPHERIC PRESSURE

Martin[844]		Iwase[572]	
Temperature, °C.	Solubility, cu. cm. of H_2 per 100 g. iron	Temperature. °C.	Solubility, cu. cm. of H_2 per 100 g. iron
. . . .	. . . .	200	1.685
. . . .	. . . .	300	3.600
440	0.30	410	5.120
522	0.75	520	6.980
649	1.49	658	9.285
772	2.10	740	11.065
. . . .	. . . .	800	11.925
896	2.83	900	13.325
924	4.46	920	14.635
1005	5.35	1010	26.200
1087	6.78	1080	34.600
1159	7.13		

molecules, at ordinary temperatures. Measurements of the rate of diffusion of hydrogen through open-hearth iron by Lewkonja and Baukloh[1014] have shown a continuous increase in the diffusion rate with increasing temperature between 700 and 1000°C. No sudden change, corresponding to the increase in solubility at the alpha-gamma transformation reported by Sieverts and by Martin, was observed. At 740°C. hydrogen diffused through the 1-mm. wall of the closed cylindrical diffusion specimen at the rate of 0.5 cu. cm. per hr. At 1000°C. the rate was 16 cu. cm. per hr. The rate of increase with increase in temperature above 900°C. was much greater, however, than the rate in the lower part of the temperature range. The conclusion was also reached that the temperature rate of diffusion was dependent upon grain size. A diffusion rate of 2 cu. cm. per hr. was obtained at 850°C. for open-hearth iron having a grain size (average cross-sectional area) of $3000\mu^2$ ($\mu = 0.001$ mm.), whereas in a similar set-up in which the iron had a grain size of $7000\mu^2$, the diffusion rate was approximately 0.75 cu. cm. per hr. This is evidently to be interpreted as a greater tendency for hydrogen to diffuse along the grain boundaries than through the body of the grains.

Pfeil[682] demonstrated conclusively that a loss of tensile strength is produced in iron by atomic hydrogen and that the fracture is intercrystalline.   He also concluded that hydrogen in iron decreased the cohesion across the cubic cleavage planes of the crystal.   The material used was decarburized mild steel containing 0.064 per cent silicon, 0.034 per cent sulphur, 0.46 per cent manganese, and 0.02 per cent phosphorus.   The number and distribution of inclusions in such material seem to have an important bearing on the degree of brittleness produced by hydrogen.[588]

Some diffusion of atomic hydrogen out of iron occurs at room temperature and, according to Pilling,[485] the diffusion of hydrogen from electrolytic iron upon heating becomes distinctly noticeable at 100°C. and reaches its maximum around 200°C. Pilling observed a pronounced increase in the scleroscope hardness of electrolytic iron after heating to approximately 250°C. Indications of a second increase in the rate of gas evolution between 600 and 700°C. were also reported.

By means of thermal analysis Rawdon and his associates[683] showed that open-hearth iron which had been made the cathode of an electrolytic cell and therefore contained atomic hydrogen behaved differently from iron which had been heated in hydrogen gas above the A_3 transformation.   Evidently the latter material retains some hydrogen upon cooling and presumably certain irregularities in the subsequent behavior upon heating can be associated with this.   An evolution of heat having its maximum between 300 and 400°C. was observed, as well as irregularities in the expansivity curve in the same temperature range.   On the other hand, iron charged with atomic hydrogen showed an absorption of heat having its maximum at approximately 200°C.   This was particularly true for iron which had been reduced from the oxide and then charged with atomic hydrogen. Wever and Pfarr[1038] showed that electrolytic pickling caused an appreciable distortion of the lattice of alpha iron.

The existence of definite "hydrogen points," below the A_2 transformation in high-purity iron, reported by Roberts-Austen[90] on the basis of thermal analysis of electrolytic iron, was not confirmed by Rawdon and his associates or by Baker.[189] Likewise, the embrittlement of a low-carbon steel, reported by Heyn[94] as produced by hydrogen, which was retained by

quenching the hot metal directly into water from a hydrogen atmosphere at a temperature above A_3, has not been confirmed for high-purity iron. Data reported recently by Luckemeyer-Hasse and Schenck[1017] for ingot iron indicated a greater notch brittleness for the iron quenched after being heated in hydrogen than for the same material quenched after being heated in a vacuum. No appreciable difference in hardness was observed, however.

According to Esser and Cornelius,[995] the presence of hydrogen in iron resulted in a peculiar "doubling" of the A_3 transformation although otherwise the transformation temperatures were not affected. The same phenomenon was previously observed by Harrington and Wood[889] and was considered by them to be characteristic of pure iron rather than to be the effect of any hydrogen present.

There is still considerable uncertainty as to the real nature of iron-hydrogen solutions largely because iron of high purity has rarely been used in the studies made. In Hüttig's classification[670] of the hydrogen-metal combinations, iron is classed with the metals which form "hydrides" which closely resemble alloys in their nature especially at low temperatures. Borelius[701] has put many of the data obtained by Sieverts into the form of mathematical equations as has Lombard[727] for the rate of flow of hydrogen under pressure through an iron wall. No satisfactory equilibrium diagram has as yet been proposed for the iron-hydrogen system. The effect of hydrogen on the magnetic properties of iron was discussed in Chapter VII.

260. Manganese.—The critical review by Krivobok and Wells[1012] of the existing data, including their own,[1013] and the related work of Walters and associates,[987] on the constitution of iron-manganese alloys shows the uncertainty which exists concerning this system. However, manganese enters readily into solid solution in iron, and for small amounts of this element the essential facts may be said to be well established.

Above 1400°C., iron containing manganese up to approximately 2 per cent[337] exists in the delta condition, characterized by a body-centered cubic lattice. The temperature of A_3 is rapidly lowered with increasing manganese content but on account of the marked hysteresis on heating and on cooling,[604,891,900] the alpha-gamma transformation appears to be

spread over a considerable range instead of occurring at a definite temperature. The existence of a second phase[857] at temperatures of approximately 400°C. and below in alloys containing somewhat more than 10 per cent of manganese adds to the complexity. According to Esser and Oberhoffer,[604] the temperature of the A_2 transformation is lowered linearly by increasing manganese content and occurs at 690°C. in iron having a manganese content of 2.2 per cent.

The limit of solid solution of manganese in iron at room temperature has not been definitely established. Schmidt[857] reported it to be approximately 10 per cent; X-ray examination of an alloy containing 10.08 per cent manganese (plus 0.03 per cent carbon) showed only one phase present, whereas the existence of two phases was clearly shown in a comparison alloy containing 11.8 per cent. According to Schmidt, the parameter of the body-centered lattice of alpha iron is increased 0.28 per cent by the introduction of 10 per cent manganese, the relation between the parameter and the manganese content being a linear one.

261. Molybdenum.—A great many of the basic facts relating to the constitution of iron-molybdenum alloys can be credited to Sykes.[687] Although Takei and Murakami[862] and Arnfelt[761] differ in some of their conclusions, these differences relate especially to the alloys of intermediate and high molybdenum content. At room temperature iron can hold about 6 per cent molybdenum in solid solution. With increasing temperature, the solubility limit does not change greatly until the temperature exceeds 600°C., after which it increases, and at 1440°C. iron can hold 24 per cent of molybdenum in solution according to Sykes, and 38 per cent according to Takei and Murakami. Molybdenum is one of the elements which lower the temperature of the A_4 transformation and raise A_3, thus forming an inclosed gamma field in the diagram. The maximum amount of molybdenum which can be retained in solution in gamma iron is about 3 per cent. The temperature of the A_2 transformation is lowered only very slightly by molybdenum according to Takei.[862] The equilibrium diagram for the system iron-molybdenum is discussed in detail in another monograph[969] of this series.

The introduction of molybdenum into alpha iron does not change the type of lattice structure and the increase in the

parameter of the body-centered cubic lattice is very small. According to Chartkoff and Sykes[874] the addition of molybdenum to saturation expanded the lattice 1.3 per cent.

262. Nickel.—In spite of the numerous studies which have been carried out on iron-nickel alloys, there is still considerable uncertainty as to certain portions of the system, particularly the alloys having a nickel content from 20 to 40 per cent. The effect of a small amount of nickel is well understood, however, and the excellent summary by Merica[1019] of the constitution of iron-nickel alloys based upon existing technical information has been used as a basis of discussion here.*

At high temperatures, nickel enters into solid solution in iron in all proportions. Above 1400°C. the delta solid solution is the stable form with a nickel content of approximately 4 per cent or less. This solution has a body-centered cubic lattice and is similar to the stable form at room temperature. The general effect of nickel on the temperature of A_3 transformation is to lower it. However, on account of the pronounced hysteresis which exists, definite temperatures cannot be assigned with certainty for specific nickel contents. In iron containing 5 per cent, hysteresis is observed within the temperature range 600 to 750°C. Above this range, the gamma solid solution is stable, and below it the alpha solid solution is stable. The substitution of nickel atoms for iron in the lattice does not change the parameter greatly; it varies from 2.86 Å. for iron to 2.875 Å. for the solid solution containing 32 per cent nickel. The effect of nickel on the A_2 transformation is uncertain; within the field of the alpha solid solution, it is believed to be lowered slightly by increasing nickel content.

C. NITROGEN AND OXYGEN

263. Nitrogen.—Nitrogen is a common impurity in commercial iron which has been melted. A recent investigation[1076] indicates that, at approximately atmospheric pressure, nitrogen is soluble in molten iron to the extent of 0.039 per cent at a temperature slightly above the melting point, and 0.042 per cent at 1760°C.

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* The constitution of the iron-nickel alloys will be discussed in detail in a forthcoming monograph of this series, "The Alloys of Iron and Nickel," now in preparation.

Braune[128] was probably the first to study systematically the influence of nitrogen on iron and its structure. He showed that nitrogen was similar to carbon in its effect as a hardening and strengthening element and, if present in sufficient amount, resulted in a microstructural constituent analogous to the carbon-bearing constituent pearlite. The name braunite is often used in referring to the nitrogen-bearing constituent which is essentially an eutectoid of iron with a compound of iron and nitrogen. The limit of solubility of nitrogen in iron is usually not exceeded unless the metal has been subjected to unusual conditions. Nitrogen in slight excess over this limit shows itself as "nitride needles" within the individual ferrite grains, as in arc-fused metal in welds.[418] The term "needle" is a misnomer, since the particles are in reality flat plates seen in cross section.

According to the work of Sieverts and his associates,[859] which has been confirmed by Martin,[844] the solubility of nitrogen in gaseous form in iron is very slight up to the temperature of the A_3 transformation. As the iron assumes the gamma form the solubility increases greatly, the volume of nitrogen in 100 g. of metal being of the order of 16 cu. cm. (measured under standard conditions) with a slight decrease in solubility with increase in temperature above A_3. Iwase's[672] results confirmed Sieverts' in showing a difference in the solubility in alpha and in gamma iron. He noted no sudden increase at A_3, however, but merely a more rapid rate of absorption of nitrogen with increasing temperature above this point. Alpha iron takes up nitrogen from "cracked" ammonia and this is the means used to obtain materials for the study of the equilibrium diagram.

The diagram of the iron-nitrogen system, as it is known at present, is to be attributed largely to the work of Fry[509] and of Sawyer.[531] There are still many points to be settled concerning the high-nitrogen alloys, but the main facts relating to the occurrence of relatively small quantities of nitrogen in iron and the attendant effects are well established. According to Fry, the temperature of the A_2, or magnetic, transformation is lowered slightly by nitrogen from 768 to 740°C. within the solid-solution field. The temperature of the A_3 transformation of the system decreases with progressive increase of nitrogen until the eutectoid temperature is reached. The recent work of Lehrer[895] places the temperature of this eutectoid at 591°C.

with a nitrogen content of 2.35 per cent instead of Fry's values of 580°C. and approximately 1.5 per cent nitrogen. The maximum amount of nitrogen which alpha iron can hold in solid solution occurs at this temperature, the amount according to Fry[509] being 0.5 per cent. The recent precise measurements by X-ray methods of Eisenhut and Kaupp,[878] who used the Debye-Sherrer method on carbonyl iron in powder form, gave 0.42 per cent nitrogen as the maximum solid solubility of nitrogen and 591°C. as the eutectoid temperature. Determinations by the same investigators have shown solubility limits at different temperatures as follows: 450°C. 0.32 per cent, 620°C. 0.39 per cent, and 700°C. 0.34 per cent. The limit at room temperature has not been determined so precisely. Sawyer[531] gave a value of 0.3 per cent based upon microscopic studies showing whether or not nitride needles were present in the grains. The value given by Fry,[509] 0.15 per cent nitrogen, probably is more nearly correct. The rate of increase in solubility of nitrogen in iron with increasing temperature is much greater above 450°C. than below this temperature according to Fry. The results obtained by Dean and his associates[818] on the dispersion hardening of nitrided electrolytic iron by reheating it after it had been quenched confirm this finding. The hardness (Rockwell *B*) of remelted electrolytic iron with nitride needles apparent in the microstructure was increased from 42 to 70 by quenching from 500°C.; on standing at room temperature, a further increase in hardness up to 93 occurred, which value did not fall below 90 on heating the material at 100°C.

According to Eisenhut and Kaupp,[878] within the limit of solid solubility the body-centered lattice of iron is changed only slightly by the presence of nitrogen. Measurements at 620°C. gave 2.865 Å. for a lattice parameter for iron containing 0.25 per cent nitrogen; 2.87 Å. for 0.34 per cent nitrogen, and 2.872 Å. for 0.4 per cent nitrogen, the value for iron containing no nitrogen being 2.86 Å. Several investigators have reported upon the structure of the iron-nitrogen compounds.[850,878,888,890] A discussion of the nitrogen-rich alloys is not necessary for an understanding of nitrogen as an impurity in iron. All investigators agree on the existence of at least two compounds, Fe_4N and Fe_2N; the former occurs in needle form or as an eutectoid when the solubility limit of nitrogen in iron is exceeded. The

work of Epstein and associates[822] indicated the existence of three distinct compounds, and Fe_6N was suggested by him as the needle-like constituent in the structure of nitrogen-bearing iron. This has not been confirmed, however, by later workers.[895] Mehl and his associates[1063] recently explained the mechanism of the precipitation of Fe_4N from the saturated solution of nitrogen in alpha iron, as it relates to the crystal structure. Fe_4N, precipitating from the solid solution, takes the form of lenticular plates which lie parallel to the (2 1 0) planes of the alpha iron matrix. The general plane of the Fe_4N plate is the (1 1 2) plane of its crystal structure. Thus, the (2 1 0) plane of the iron matrix and the (1 1 2) plane of the nitride precipitate coincide, "with the close-packed strings of atoms in the two planes mutually parallel."

The presence of nitrogen in the metal has been shown to be the principal cause of embrittlement in certain welded joints.[928] According to Scott,[941] nitrogen has about four times the effect of the same amount of phosphorus on the properties of steel; an increase of 0.01 per cent in the nitrogen content was sufficient to cause a marked difference in physical properties, but the average amount of nitrogen (0.0045 per cent) found in open-hearth steel was not seriously detrimental to the quality. Ehn[923] concluded that the change in mechanical properties due to nitrogen was similar to that caused by carbon but was not so pronounced. He mentioned the embrittling action and the injurious effect on magnetic properties as a result of nitrides. Such effects are intensified by the tendency of the nitride to segregate; it was reported by Diergarten and Eilender[920] that the nitrogen content of the center and upper parts of an ingot, of low-carbon basic open-hearth steel, may be 100 per cent higher than in the outer parts of the ingot.

264. Oxygen.—The complete elimination of oxygen from iron prepared by thermal means is extremely difficult. In iron which is otherwise pure, most of the oxygen that is present occurs as discrete globules of FeO, gray in color, and usually having a diameter sufficiently large to render them visible in a polished microsection.

A small amount exists in solid solution, but the limit of solid solubility at room temperature is still uncertain. Tritton and Hanson[585] set this limit as about 0.05 per cent of oxygen.

Gillett,[871] however, stated that metallographic examination showed it to be much lower than 0.05 per cent; Ellis and Schumacher[1052] placed it at 0.01 per cent; and Esser and Cornelius[996] believed that oxygen was insoluble in solid iron, but this conclusion was based on microscopic evidence which appears to be incomplete. The solubility of oxygen in iron increases as the temperature is increased. Krings and Kempkens[557] announced that the limit of solubility at 715°C. is 0.11 ± 0.015 per cent. The value of 0.21 per cent obtained by Tritton and Hanson[585] for the limit of solubility of oxygen in liquid iron at the melting point is in good agreement with the value obtained by others[719] and is generally accepted. Herty and his associates[719] determined the solubility in liquid iron up to a temperature of over 1700°C. They found a linear relationship between temperature and solubility limit, the value for 1600°C. being 0.305 per cent oxygen and that for 1700°C. 0.45 per cent. Two immiscible layers formed when the concentration of oxygen in liquid iron exceeded these values. According to Tritton and Hanson[585] the presence of 0.20 per cent oxygen caused the melting of iron to be spread over a range of 10°C.

The influence of oxygen on the transformations in iron is still uncertain although Tritton and Hanson[585] detected no change in the A_3 and A_2 transformations in iron containing 0.12 to 0.21 per cent oxygen. A suggestion by Oberhoffer[733] that the presence of oxygen in iron may result in the formation of a closed gamma loop in the constitutional diagram, as many other additions do, has not been followed up in an experimental way. Yensen,[871] reasoning somewhat along this line from the results obtained with irons containing varying amounts of silicon and carbon, advanced the theory that *pure* iron should show no allotropic points whatsoever. Gillett in discussion of Yensen's paper presented some results on the thermal analysis of supposedly pure iron, obtained by hydrogen reduction of oxidized electrolytic iron, which indicated that the apparent absence of the A_3 and A_2 transformations in this material did not necessarily show that the iron was transformationless. Some of the hydrogen-reduced sponge iron contained 10 to 11 per cent oxygen, and the insulating action of the film inclosing the individual particles of iron was considered to be the cause of the lack of the thermal effect accompanying the A_3 change.

The best compilations of data in the form of iron-oxygen constitutional diagrams are those of Mathewson and associates[930] and of Benedicks and Löfquist.[765] Both show very good agreement in the portion covering the iron-rich alloys.

Contrary to the usual opinion, oxygen in iron does not appear to render it red short in rolling. Although Austin[324] experienced some difficulty in the hot working of iron containing oxygen, Tritton and Hanson[585] and Herty[719] reported that iron which contained as much as 0.08 per cent but was low in sulphur (less than 0.01 per cent) could be worked without difficulty. According to Fell,[925] however, oxygen occurring simultaneously with sulphur in iron appears to accentuate the influence of sulphur in producing red shortness. Reschka[981] investigated the properties of compressed and sintered (but not melted) alloys of high-purity iron with oxygen and concluded that hot working was possible with oxygen contents up to 3 per cent; manganese oxide reduced hot deformation more than did ferrous oxide; ferrous sulphide reduced the forgeability; the tensile strength of ferrous oxide alloys increased with increasing oxygen up to 0.2 per cent; and the toughness decreased with increasing oxygen content.

The presence of oxygen affects the grain size of heat-treated iron, according to Gries and Esser,[781] the structure, according to Grossmann,[832] and the hardenability, according to Bain.[957]

D. PHOSPHORUS TO ZINC

265. Phosphorus.—A great deal of study has been devoted to phosphorus as an impurity in steel and iron since the early work of Percy in 1864, but the principal facts concerning the constitutional diagram of the iron-phosphorus system have been established only comparatively recently. Most of this knowledge is to be credited to Haughton,[718] who repeated the earlier work of Stead,[99,394] Saklatwalla,[184] and Konstantinow[215] and established with precision the limit of solubility of phosphorus in iron and its effects upon the transformations as well as the other important points in the alloy system up to a concentration of 32 per cent phosphorus.

Phosphorus exists in solid solution in iron at room temperature, the limit of solubility being slightly less than 1 per cent according to Haughton[718] although the X-ray studies of Oberhoffer and

Kreutzer[800] suggest a somewhat higher limit, 1.7 per cent. On the other hand, Yensen[590] interpreted some observations of the effect of phosphorus on the magnetic properties of iron as indicating that solubility at room temperature did not exceed 0.015 per cent. The range of solid solubility is changed very little with increasing temperature and is 1.1 per cent at A_2, the temperature of which is lowered slightly to 745°C. The maximum solubility, 2.8 per cent, occurs at 1050°C. The A_4 transformation is lowered by phosphorus and A_3 is raised; the resulting gamma loop extends to a phosphorus content of 0.5 per cent.

With phosphorus much above 1 per cent, a second phase, a compound Fe_3P, corresponding to 15.7 per cent phosphorus, occurs in increasing amounts with increasing phosphorus content.

Phosphorus in solid solution in iron often results in a characteristic "hazy" cellular pattern in the microstructure within the ferrite grains after etching. This is most pronounced when an etching reagent containing copper has been used. The marked persistence of this pattern after the material has been annealed is indicative of a very slow rate of diffusion of phosphorus through the iron. According to Whiteley,[458] differences in phosphorus content of less than 0.02 per cent in adjacent parts of otherwise technically pure iron can be readily shown by means of a cupric etching reagent.

266. Platinum.—According to the early work of Isaac and Tammann,[159] iron forms a continuous series of solid solutions with platinum at high temperatures; at room temperature platinum is soluble in alpha iron to the extent of nearly 50 per cent.

267. Silicon.—Silicon is a common impurity in iron. As a basis for the discussion of this impurity the monograph "The Alloys of Iron and Silicon"[1000] will serve admirably. Although there is still considerable uncertainty concerning the iron-rich alloys of this system, many of the principal facts seem to have been well established. Silicon exists in solid solution in iron at room temperature up to approximately 15 per cent. Whether or not this is a simple homogeneous series of solutions is in doubt. The presence of carbon and oxygen appears to be largely responsible for the irregularities noted in the alloys relatively low in silicon, 0 to 5 per cent. Up to 900°C. the solubility limit is not essentially affected by an increase in temperature.

Silicon lowers the temperature of the A_4 transformation in iron and raises that of A_3 and thus, with progressively increasing amounts up to approximately 2 per cent, results in the formation of a closed gamma loop. The retention of iron in the gamma state at high temperature by the presence of silicon, therefore, is limited and is dependent upon the silicon content. The temperature of the A_2 transformation is lowered by an increasing silicon content and at the limit of solubility, 15 per cent silicon, is in the neighborhood of 490°C.
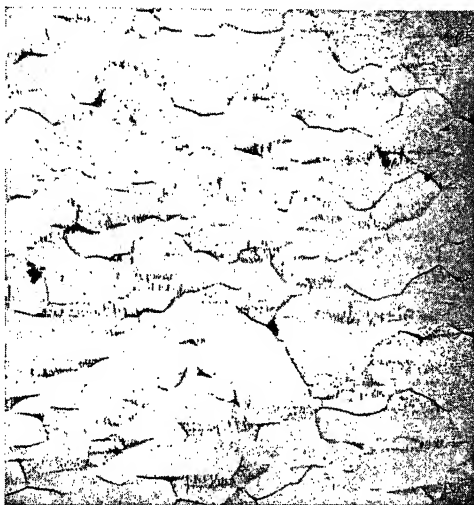
FIG. 110.—Grain boundaries and other markings on the polished surface of a 4 per cent silicon-iron alloy, revealed by a suspension of magnetic Fe_2O_3 in alcohol while the specimen was in a magnetic field. Actual size. (*Bitter.*[993])

Probably the most important effect of silicon on iron relates to the magnetic properties. In studying the nature of ferromagnetism, Bitter[959,993] has shown that a crystal of a ferromagnetic metal appears to behave as a conglomerate rather than as a single unit when in a magnetic field. This is well shown by the iron-silicon solid solutions although the results for commercially pure iron do not differ essentially from those for iron containing a small amount of silicon. Figures 110 and 111 are representative of the results obtained with iron containing

4 per cent of silicon. The real significance of these results has not yet been fully established.

268. Sulphur.—Sulphur, as an impurity in iron and steel, has been the subject of a great deal of study, the best compilations on the subject being those of Wohrman[812] and of Benedicks and Löfquist.[918] The first important published work on the equilibrium diagram of the iron-sulphur system was that of Treitschke and Tammann,[151] who showed that iron and iron sulphide form a simple eutectiferous system, the eutectic con-

Fig. 111.—Grain markings in silicon-iron (4 per cent silicon) revealed as in Fig. 110. Note the different orientations of the three grains. Approximately 10 ×. (*Bitter.*[959])

taining about 15 per cent of metallic iron. Friedrich[211] showed that the conclusion of Treitschke and Tammann, that molten iron and iron sulphide are not miscible in all proportions, was not correct and established the diagram in essentially the form used today, the eutectic temperature being given as 983°C. and the eutectic composition as 15 per cent iron. Loebe and Becker[261] confirmed these results and· in addition concluded that sulphur does not enter into solid solution in iron and that the transformation points of iron are unaffected. The recent work of Miyazaki[797] who took precautions to prevent contamination of the materials used with oxide has not greatly changed

the diagram. He placed the eutectic at 17 per cent iron, the eutectic temperature remaining unchanged from the value set by Loebe and Becker, 985°C. On the basis of results of electric-resistivity measurements, Miyazaki concluded that the limit of solid solubility at the eutectic temperature is less than 1 per cent iron sulphide and at room temperature must be very small indeed since microscopic examination of iron containing 0.05 per cent iron sulphide (0.018 per cent sulphur) revealed numerous discrete particles of the sulphide in the microstructure. Ellis and Schumacher[1052] concluded that 0.015 per cent is the probable limit of solubility at room temperature. In the absence of manganese, the identification of sulphide in the microstructure of iron is readily made by the brownish yellow color of the sulphide particles and the fact that they are readily attacked by a boiling alkaline solution of sodium picrate.[367]

269. Tin.—Tin enters into solid solution in iron to a limited extent. When a clean surface of iron is maintained in contact with tin at a high temperature, the tin diffuses into the iron. Evidence of this in the microstructure of the iron is shown principally by a surface layer of columnar grains consisting, presumably, of the alpha solid solution. The magnitude and rate of diffusion are shown in the results obtained by Bannister and Jones[916] and presented in Table 95. The limit of solid solu-

TABLE 95.—DIFFUSION OF TIN INTO IRON*

Period, hr.	Temperature, °C.	Depth of diffusion, in.
3	950	0.0093
6	950	0.0133
12	950	0.0189
24	950	0.0251
6	1000	0.0176
4	1050	0.0184
2	1100	0.0169

* Bannister and Jones.[916]

bility of tin in iron at room temperature is in doubt. Edwards and Preece[922] found the limit at 300°C. to be 10 per cent, with indication of a decrease in solubility at lower temperatures, which would mean a lower value than the 13 per cent reported by Wever and Reinecken[641] for room temperature. The maxi-

mum solubility of tin in iron occurs at 760°C.[922]   Wever and Reinecken[641] found that tin has a limited solubility in gamma iron.   The temperature of the A_4 transformation was reported to be lowered about 140°C. for each one per cent of tin and that of the A_3 transformation raised 40°C. by the same amount, the result being a closed gamma field with a maximum width corresponding to approximately 2 to 3 per cent tin.

The temperature of the A_2 transformation in iron is not affected by the presence of small amounts of tin.

270. Titanium.—Information on the effect of titanium on iron is meager.   Wever[810] included titanium in the list of elements whose presence in iron results in a closed gamma field, without any supporting published data, however.   Some evidence in favor of Wever's statement was secured by Michel and Bénazet[898] on a low-carbon steel (0.1 per cent carbon) treated with titanium which was not entirely free from aluminum.   Their data roughly suggested a maximum solubility of titanium in gamma iron of approximately 1 per cent.   The limit of solubility of titanium in alpha iron at room temperature has not been accurately determined.   The early work of Lamont[285] placed the limit of solid solubility as 6.3 per cent at the eutectic temperature, 1300°C.   Wasmuht[951] showed that iron having a titanium content of 3 per cent could be hardened by a precipitation treatment, but only if another element, such as nickel or silicon, was present.   The results obtained by Seljesater and Rogers[982] with iron-titanium alloys, made from ferrotitanium which contained substantial amounts of aluminum and silicon, led these authors to conclude that approximately 3 per cent of titanium was the limit of solid solubility at room temperature.

271. Tungsten.*—The effect of small amounts of tungsten on iron is similar to that of corresponding amounts of molybdenum.   The solid-solubility limit of tungsten in iron, as determined by Honda and Murakami,[371] was redetermined by Sykes.[688]   At a temperature just below the melting point of iron, about 33 per cent of tungsten is soluble in iron and about 8 per cent at room temperature.   The introduction of tungsten into the body-centered cubic lattice of iron to the saturation value, 33 per cent, increases the parameter about 1.05 per cent.

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* Full discussion of the effect of tungsten in iron is found in another volume[1054] of this series of monographs.

The increase resulting from 4 per cent of tungsten was not detectable and 10 per cent caused an increase of about 0.2 per cent in the lattice parameter.[874]

The solubility of tungsten in gamma iron, like that of molybdenum, is limited, only 3 per cent being completely soluble although the duplex gamma-alpha field extends to 6 per cent.[947] A closed gamma loop results from the lowering of the temperature of the A_4 transformation and the raising of A_3.

272. Vanadium.—The available data on the constitution of iron-vanadium alloys have recently been critically reviewed by Saklatwalla and Strauss.[1023] Although there is considerable uncertainty on some points, the main facts are well established. Iron dissolves vanadium in all proportions in solid solution at high temperatures. At room temperature the solubility of vanadium in iron is limited to approximately 25 per cent. With a vanadium content much above this, a second phase, a compound, FeV, appears.

The introduction of vanadium in small amounts into iron results in the raising of A_3 and the lowering of the A_4 transformation and thus creates a restricted gamma-iron field or loop. The maximum amount of vanadium which can be dissolved in gamma iron is about 1.1 per cent. All available data indicate a slight increase in the temperature of the magnetic or A_2 change with increase of vanadium content; 785°C. for 1.4 per cent vanadium has been given by Wever and Jellinghaus.[912] The effect of greater and increasing amounts of vanadium is still not fully determined.

The parameter of the body-centered cubic lattice of iron is only very slightly increased by the introduction of small amounts of vanadium. Wever and Jellinghaus[912] found an increase of 0.17 per cent for iron containing 13.4 per cent of vanadium.

273. Zinc.—Information on iron containing small amounts of zinc is very meager. Zinc is not ordinarily considered as an impurity in iron. Alloys of iron having a very low zinc content can be prepared only under pressure in closed containers.[289] Zinc is classed by Wever[810] as one of the elements the addition of which to iron results in a widening of the gamma field. This is consistent with the published equilibrium diagram[851] which shows a continuous lowering of the A_3 temperature to approxi-

mately 620°C. with progressively increasing zinc content up to 18 per cent.

According to Osawa and Ogawa[851] iron at room temperature can retain approximately 18 per cent of zinc in solid solution. The X-ray measurements of these investigators indicate that the increase in the parameter of the body-centered lattice of alpha iron with progressively increasing amounts of zinc is not a linear relationship. An increase of 0.73 per cent was noted in the parameter of the lattice of the solid solution containing 14 per cent zinc, whereas an addition of 2.6 per cent of zinc resulted in an increase in the lattice parameter of 0.49 per cent.

The temperature of A_2 is lowered slightly by the presence of zinc. According to Osawa and Ogawa[851] it occurs at approximately 740°C. in iron containing 10 per cent zinc.

E. MISCELLANEOUS CONSTITUENTS

The alkali metals and the alkaline-earth metals, including magnesium, are insoluble in iron.[810] Likewise, bismuth,[158] lead,[158] and silver[164] have been stated to be insoluble in iron. Petrenko[164] reported that up to a temperature of 1600°C. he was unable to detect any solubility of silver in iron. According to Burgess and Aston,[274] however, silver is slightly soluble. They found that 0.69 per cent was the maximum amount of silver retained by molten electrolytic iron although the preparation of alloys with an intended silver content of 10 per cent was attempted. Further work on the solubility of silver in iron by the more precise methods now available is very desirable. Zirconium, according to Wever,[810] is one of the elements, the solubility of which in gamma iron is limited and which, therefore, form a closed gamma field. Supporting experimental data were not given.

The influence of the different elements on the transformations in iron was discussed by Wever.[810] Figure 112 from his paper is representative of the correlations made. Although the plotted data will not support any sweeping generalization, certain important trends are observed. It will be noted (Fig. 112) that all the elements whose insolubility in iron is well established have an atomic volume considerably greater than that of iron. With the exception of carbon and nitrogen, all the elements which are favorable to maintaining the gamma phase in iron

possess an atomic volume which differs very slightly from that of iron. With the notable exception of beryllium and boron, both of which have atomic volumes less than that of iron, the elements which tend to narrow the gamma field, *i.e.*, are unfavorable to its maintenance, have atomic volumes which are definitely although slightly greater than that of iron. Cadmium and silver appear to be exceptions. Wever has shown that, if the
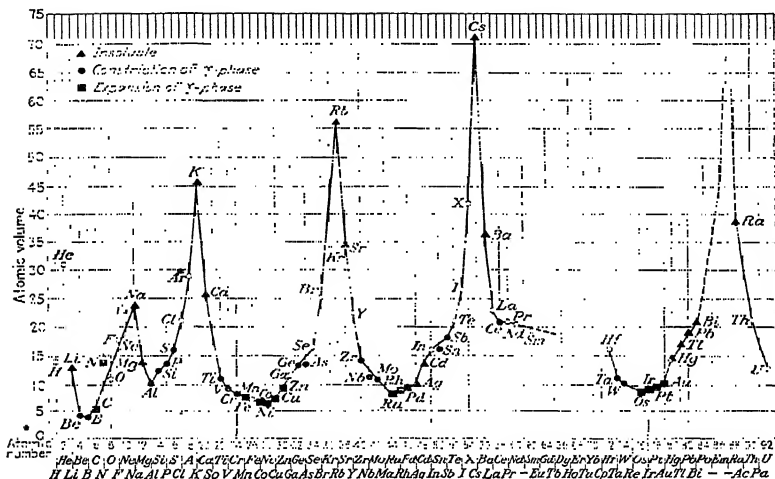
FIG. 112.—The solid solutions of iron with other elements arranged in the order of atomic volumes. (*Wever*.[810])

comparison is made on the basis of atomic radius instead of atomic volume, the resulting curve is entirely analogous. Figure 113, from Wever's paper,[810] in which the character of the iron-rich alloys formed by different elements is shown with respect to the position of the elements in the periodic table, supports the general conclusions expressed above.

F. AUTHORS' SUMMARY

The effect of minor constituents on the properties of iron, and the minimum concentration of minor constituents which produces a noticeable effect, vary too widely to permit general conclusions. Variation is evident not only in the effect of

Row	I a	I b	II a	II b	III a	III b	IV a	IV b	V a	V b	VI a	VI b	VII a	VII b	VIII a	b
I														1H		2He
II		3Li ▲	4Be ●			5B ○		6C ◻		7N ◻		8O		9F		10Ne
III		11Na ▲	12Mg ▲			13Al ●		14Si ◻		15P ●		16S ○		17Cl		18A
IV	19K ▲	29Cu ◻	20Ca ▲	30Zn ◻	21Sc	31Ga ●	22Ti ●	32Ge ●	23V ●	33As ●	24Cr ●	34Se	25Mn ◼	35Br	26Fe ◼ 27Co ◼ 28Ni ◼	36Kr
V	37Rb ▲	47Ag ▲	38Sr ▲	48Cd ▲	39Y	49In	40Zr ○	50Sn ●	41Cb ●	51Sb ●	42Mo ●	52Te	43Ma	53I	44Ru ◼ 45Rh ◼ 46Pd ◼	54X
VI	55Cs ▲	79Au ◻	56Ba ▲	80Hg ▲		81Tl ▲	58Ce ○	82Pb ▲	73Ta ●	83Bi ▲	74W ●	84Po	75Re	85–	72Hf 76Os ◼ 77Ir ◼ 78Pt ◼	86Em
VII	87–		88Ra ▲		89Ac		90Th		91Pa		92U					

▲ Insoluble   ● Constriction of γ-phase   ◼ Expansion of γ-phase   ○ Unknown

Fig. 113.—The solid solutions of iron with other elements arranged in the order of the periodic system.   (*Wever*,[810])

different constituents on a single property of iron but also in the effect of a single constituent on different properties. Each of the sections of this chapter constitutes a condensed summary of the effect of a single minor constituent, with particular emphasis on the physical condition of the constituent as it exists in the metal.

APPENDIX

CONDENSED SUMMARY OF THE PROPERTIES OF IRON

The following tabulation is a condensed summary of the best available information of those properties of iron which can be conveniently expressed in simple terms. Some of these values probably represent the properties of absolutely pure iron, at least within the limits of error of the available determinations; other values perhaps approximate the values for the properties of absolutely pure iron, but the degree of approximation remains to be determined.

Atomic number = 26
Atomic weight = 55.84
Isotopes = 56 and 54
Valence = 2 and ·3
Density at 20°C. = 7.87 g. per cu. cm.
Melting point = 1535°C. (2795°F.)
Boiling point = approximately 3000°C. (5430°F.)

Transformations:

A_4 (gamma-delta) = 1400°C. (2550°F.)
A_3 (alpha-gamma) = 910°C. (1670°F.)
A_2 (magnetic transition in alpha iron) = about 770°C. (1420°F.)

Structure:

Alpha iron = body-centered cube
Lattice constant at 20°C. = 2.861 Å.
Gamma iron = face-centered cube
Lattice constant at the A_3 point = 3.64 Å.
Delta iron = body-centered cube
Lattice constant at the A_4 point = about 2.92 Å.

Thermal properties:

Heat of fusion = 65 cal. per g.
Heat effect at the A_2 point = probably none
Heat effect at the A_3 point = 3.86 cal. per g.
Heat effect at the A_4 point = 1.7 cal. per g.
Volume change at the A_2 point = none
Volume change at the A_3 point = contraction for change from alpha to gamma
Volume change at the A_4 point = expansion for change from gamma to delta.

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Volume change at the melting point = expansion of less than 5 per cent for change from solid to liquid iron

Thermal conductivity at 0°C.   ː 0.19 cal. per sec. per sq. cm. (°C. per cm.)

Electric properties:

Resistivity at 20°C. = 9.8 microhm-cm.
Temperature coefficient of resistivity between 0 and 100°C. = 0.0065 per °C.

Magnetic properties of a single crystal of *pure* iron:

Coercive force   = probably zero
Hysteresis loss   = probably zero
Maximum permeability = 500,000 or more

Mechanical properties of polycrystalline electrolytic iron, vacuum-fused:

Tensile strength   = 35,000 to 40,000 lb. per sq. in.
Yield strength   = 10,000 to 20,000 lb. per sq. in.
Elongation   = 30 to 60 per cent
Reduction of area = 70 to 90 per cent
Brinell hardness   = 60 to 70
Endurance limit   = 15,000 to 40,000 lb. per sq. in.
Young's modulus   = about 30,000,000 lb. per sq. in.

BIBLIOGRAPHY

1827–1850

1. FISCHER, N. W.: Über Metallreductionen durch andere Metalle auf nassem Wege (The Reduction of Metals from their Solutions by Other Metals), *Ann. d. Phys. u. Chem.*, v. 9, 1827, pp. 255–266.
2. BECQUEREL, A. C.: Considérations générales sur les décompositions électrochimiques et la réduction de l'oxide de fer, de la zircone et la magnesie, à l'aide de forces électriques peu énergiques (General Considerations on Electrochemical Decomposition and on the Reduction of Iron Oxide, Zirconia, and Magnesia with the Aid of Low-voltage Electric Currents), *Ann. Chim. et Phys.*, v. 48, 1831, pp. 337–353.
3. PELIGOT, E.: Sur un moyen ·d'obtenir certains métaux parfaitement purs (A Method of Obtaining Certain Metals Perfectly Pure), *C. R. Acad. Sci.*, Paris, v. 18, 1844, pp. 670–671.
4. BOCKBUSCHMANN, M., and M. LIET: Über die Darstellung 'reinen Eisens auf galvanoplastischem Wege (The Preparation of Pure Iron by the Galvanoplastic Method), Abstracted in *Dinglers Polytech. J.*, v. 100, 1846, pp. 75–76.
5. BÖTTGER, R.: Über die Gewinnung reinen Eisens in cohärenter Gestalt mittelst Galvanismus (The Production of Pure Iron in Coherent Form by Means of Galvanism), *Ann. d. Phys. u. Chem.*, v. 7 (67), 1846, pp. 117–119.
6. PERSON, C. C.: Beziehung zwischen dem Elasticitätscoëfficienten der Metalle und deren latenter Schmelzwärme (Relation between the Modulus of Elasticity of Metals and Their Latent Heat of Fusion), *Ann. d. Phys. u. Chem.*, v. 15 (75), 1848, pp. 460–463.
7. RYHINER, W.: Über Eisenreduktion auf galvanischem Wege (Reduction of Iron by the Electrolytic Process), *Dinglers Polytech. J.*, v. 110, 1848, pp. 422–423.
8. POUMAREDE, J. A.: Mémoire sur quelques phénomènes de réduction; nouveaux moyens d'isoler le fer de ses combinaisons (A Memoir on Some Reduction Phenomena; New Methods for Isolating Iron from Its Compounds), *C. R. Acad. Sci.*, Paris, v. 29, 1849, pp. 518–521.
9. HAIDINGER, W.: Note über Krystalle und gestrickte Gestalten von Silber, bei dem Ausglühen des Amalgams in Schmölnitz gewonnen (Note on Crystal and Network Structure in Silver from Ignited Amalgams Produced in Schmölnitz), *Jahrbuch der k. k. geologischen Reichs-Anstalt in Wien*, v. 1, 1850, pp. 150–152.

1851–1870

10. THOMPSON, WM.: Effects of Magnetization on the Electrical Conductivity of Nickel and of Iron, *Proc. Royal Soc.* (London), ser. A, v. 8, 1857, pp. 546–550.

11. MEIDINGER, H.: Das Überziehen gravirter Kupferplatten mit Eisen auf galvanoplastischem Wege (Coating of Engraved Copper Plates with Iron by the Galvanoplastic Process), *Dinglers Polytech. J.*, v. 152, 1859, pp. 359–362.

12. BEETZ, W.: On the Molecular Changes Produced by Magnetism, *Phil. Mag.*, v. 20, 1860, pp. 458–469.

13. DeLUCA, S.: Sur la préparation du fer réduit par l'hydrogène et sur la manière de le préserver de l'oxydation (The Preparation of Hydrogen-reduced Iron and Means of Preserving It from Oxidation), *J. de Pharmacie*, v. 38, 1860, pp. 275–277.

14. KRÄMER, H.: Über das auf galvanische Wege erzeugte Eisen (Iron Produced by the Galvanic Process), *Dinglers Polytech. J.*, v. 160, 1861, pp. 444–446.

15. LE ROUX, F. P.: Recherches sur les courants thermo-électriques (Researches on Thermoelectric Currents), *Ann. Chim. et Phys.*, ser. 4, v. 10, 1867, pp. 201–291.

16. WALENN, W. H.: Electrodeposition of Iron, *Chem. News*, v. 17, 1867, p. 170.

17. KLEIN, M.: On the Electrodeposition of Iron, *Chem. News*, v. 18, 1868, pp. 133–134.

18. MATTHIESSEN, A., and S. P. SZCZEPANOWSKI: An Account of Some Experiments to Obtain Iron Free from Sulphur, *Report Brit. Assoc. Advancement Science*, 1868, pp. 342–343.

19. VARRENTRAPP, F.: Galvanische Fällung von Eisen in cohärenter Form (Electrolytic Deposition of Iron in Coherent Form), *Dinglers Polytech. J.*, v. 187, 1868, pp. 152–154.

20. GORE, G.: On a Momentary Molecular Change in Iron Wire, *Proc. Royal Soc.* (London), ser. A, v. 17, 1869, pp. 260–265. Also: *Phil. Mag.*, v. 38, 1869, pp. 59–64.

21. JACOBI, M. H.: On the Electrodeposition of Iron, *Report Brit. Assoc. Advancement Science*, 1869, p. 67. Also: *Chem. News*, v. 20, 1869, p. 102.

22. MATTHIESSEN, A., and S. P. SZCZEPANOWSKI: On the Preparation of Pure Iron, *Report Brit. Assoc. Advancement Science*, 1869, pp. 82–84. Also: *Chem. News*, v. 20, 1869, pp. 101–102.

1871–1885

23. LENZ, R.: Über einige Eigenschaften des auf galvanischem Wege niedergeschlagenen Eisens (Some Properties of Electrodeposited Iron), *Ann. d. Phys. u. Chem.*, Ergänzungsband, v. 5, 1871, pp. 242–257.

24. DRAGENDORFF, G.: Iron Reduced by Hydrogen, *Pharm. J. and Trans.*, v. 2, 1872, pp. 988–989.

25. BARRETT, W. F.: On Certain Remarkable Molecular Changes Occurring in Iron Wire at Low Red Heat, *Phil. Mag.*, v. 46, 1873, pp. 472–478.

26. CARON, H.: Note sur un nouveau procédé de trempe de l'acier (Note on a New Method of Quenching Steel), *C. R. Acad. Sci.*, Paris, v. 77, 1873, pp. 836–838.

27. ROWLAND, H. A.: On Magnetic Permeability and the Maximum of Magnetism of Iron, Steel and Nickel, *Phil. Mag.*, v. 46, 1873, pp. 140–159.

28. HOLZ, A. L.: Eine Untersuchung über Stabmagnetismus (An Investigation of Bar Magnetism), *Ann. d. Phys. u. Chem.*, v. 151, 1874, pp. 69–77.

29. VOLGER, M.: Electrodeposition of Iron, Memoir read at Frankford Society, Physical Science, Aug. 1874. Abst.: *J. Franklin Inst.*, v. 68, 1874, pp. 299–301.

30. CAILLETET, L.: Sur le fer hydrogéné (Hydrogenated Iron), *C. R. Acad. Sci.*, Paris, v. 80, 1875, pp. 319–321.

31. ROBERTS, W. C.: On the Electrodeposition of Iron, *Chem. News*, v. 31, 1875, p. 137.

32. CLASSEN, A., and M. A. VON REIS: Elektrolytische Bestimmungen und Trennungen (Electrolytic Determinations and Separations), *Ber. Deutsch. Chem. Ges.*, v. 14, 1881, pp. 1622–1633.

33. ROBERTS, W. C., and T. WRIGHTSON: Determination of the Density of Fluid Bismuth by Means of the Oncosimeter, *Phil. Mag.*, v. 11, 1881, pp. 295–299. Also: *Nature*, v. 24, 1881, p. 470.

33*A*. EWING, J. A.: Experimental Researches in Magnetism, *Phil. Trans. Royal Soc.* (London), v. 172, 1885, pp. 523–640.

34. BATTELLI, A.: Intorni all' influenza della magnetizzazione sopra la conducibilità termica del ferro (The Influence of Magnetization on the Thermal Conductivity of Iron), *Atti Reale Accad. delle Scienze, Torino*, v. 21, 1886, pp. 799–820.

35. BATTELLI, A.: Sulle proprietà termoelettriche delle leghe (The Thermoelectric Properties of Alloys), Preliminary: *Mem. Accad. Torino*, v. 36, 1885, p. 487. Final: *Atti Reale Accad. delle Scienze, Torino*, v. 22, 1886–1887, pp. 48–69; 539–556.

36. OSMOND, F.: Sur les phénomènes qui se produisent pendant le chauffage et le refroidissement de l'acier fondu (The Phenomena Which Occur during the Heating and Cooling of Steel), *C. R. Acad. Sci.*, Paris, v. 103, 1886, pp. 743–746.

1886–1890

37. NERNST, W.: Über die elektromotorischen Kräfte, welche durch den Magnetismus in von einem Wärmestrome durchflossenen Metallplatten geweckt werden (The Electromotive Force Produced by Magnetism in Metal Plates with a Heat Current Flowing through), *Ann. d. Phys. u. Chem.*, new ser., v. 31, 1887, pp. 760–789.

38. PREECE, W. H.: The Specific Resistance of Commercial Iron, *Report Brit. Assoc. Advancement Science*, v. 57, 1887, p. 609.

39. ROBERTS-AUSTEN, W. C.: The Electrodeposition of Iron, *J. Iron Steel Inst.*, 1887, I, pp. 71–74.

40. TOMLINSON, H.: Influence of Stress and Strain on the Physical Properties of Matter. III. Magnetic Induction, *Proc. Royal Soc.* (London), ser. A, v. 42, 1887, pp. 224–230.

41. WATT, A.: Electrolysis of Iron Salts, *Electrician*, v. 20, 1887–88, pp. 6; 50; 135; 185; 241.

42. JAHN, H.: Experimental-Untersuchungen über die an der Grenzfläche heterogener Leiter auftretenden localen Wärmeerscheinungen (Experimental Study of the Heat Effects at the Junctions of Heterogeneous Conductors), *Ann. d. Phys. u. Chem.*, new ser., v. 34, 1888, pp. 755–785.

43. KOHLRAUSCH, W.: Über einen Zusammenhang zwischen Magnetisirbarkeit und elektrischem Leitungsvermögen bei den verschiedenen Eisensorten und Nickel (The Relation between Magnetization and Electric Conductivity of Different Irons and Nickel), *Ann. d. Phys. u. Chem.*, new ser., v. 33, 1888, pp. 42–58.

44. BRAND, A.: Über die Anwendung von pyrophosphorsauren Doppelsalzen zur Bestimmung und Trennung von Metallen durch Elektrolyse (The Use of Double Salts of Pyrophosphoric Acid for the Determination and Separation of Metals by Electrolysis), *Z. anal. Chem.*, v. 28, 1889, pp. 581–605.

45. HOPKINSON, J.: Magnetization of Iron at High Temperatures, *Proc. Royal Soc.* (London), ser. A, v. 45, 1889, pp. 318–321.

46. RUBENS, H.: Die selective Reflexion der Metalle (Selective Reflection of Metals), *Ann. d. Phys. u. Chem.*, new ser., v. 37, 1889, pp. 249–268.

47. BALL, E. J.: On the Changes in Iron Produced by Thermal Treatment, *J. Iron Steel Inst.*, 1890, I, pp. 85–105; 1891, I, pp. 103–108.

48. OSMOND, F.: On the Critical Points of Iron and Steel, *J. Iron Steel Inst.*, 1890, I, pp. 38–71.

1891–1895

49. MOND, L., and C. LANGER: On Iron Carbonyls, *J. Chem. Soc.*, v. 59, 1891, pp. 1090–1093.

50. MOND, L., and F. QUINCKE: Note on a Volatile Compound of Iron with Carbon Monoxide, *J. Chem. Soc.*, v. 59, 1891, pp. 604–607.

51. ROBERTS-AUSTEN, W. C.: Report to the Alloys Research Committee, *Proc. Inst. Mech. Eng.*, 1891, pp. 543–604.

52. THIELE, J.: Zum Nachweis des Arsens (The Detection of Arsenic), *Liebig's Ann. d. Chemie*, v. 265, 1891, pp. 55–66.

53. DYER, H.: On the Production of Pure Iron and Steel, *J. Iron Steel Inst.*, 1892, I, pp. 88–91. Also: *Engineering*, v. 53, 1892, p. 733.

54. LANGLEY, J. W., and W. METCALF: Discussion on Structural Steel, *Trans. Am. Soc. Civil Eng.*, v. 27, 1892, pp. 383–405.

55. LYDALL, F., and A. W. S. POCKLINGTON: Magnetic Properties of Pure Iron, *Proc. Royal Soc.* (London), ser. A, v. 52, 1892–93, pp. 228–232.

56. DEWAR, J., and J. A. FLEMING: The Electrical Resistance of Metals and Alloys at Temperatures Approaching Absolute Zero, *Phil. Mag.*, v. 36, 1893, pp. 271–299.

57. LINCK, G.: Das Kristallgefüge des Eisens, studirt am Meteoreisen (Crystal Structure of Meteoric Iron), *Stahl u. Eisen*, v. 13, 1893, pp. 243–244.

58. OSMOND, F.: Discussion of Second Report to Alloys Research Committee, *Proc. Inst. Mech. Eng.*, 1893, pp. 195–198.

59. PRELINGER, O.: Zur Chemie des Mangans (The Chemistry of Manganese), *Monatsh. f. Chemie*, v. 14, 1893, pp. 353–370.

60. RICHARDS, J. W.: The Specific Heats of Metals, *J. Franklin Inst.*, v. 136, 1893, pp. 37–53; 116–131; 178–193.

61. ARNOLD, J. O.: The Physical Influence of Elements on Iron, *J. Iron Steel Inst.*, v. 45, 1894, pp. 107–155.

62. CURIE, P.: Sur les propriétés magnétiques du fer à diverses températures (The Magnetic Properties of Iron at Different Temperatures), *C. R. Acad. Sci.*, Paris, v. 118, 1894, pp. 859–862.

63. ANDREWS, T.: Micro-metallography of Iron, *Proc. Royal Soc.* (London), ser. A, v. 58, 1895, pp. 59–64.

64. CURIE, P.: Propriétés magnétiques des corps à diverses températures (Magnetic Properties of Materials at Various Temperatures), *J. de Physique*, v. 4, 1895, pp. 263–272. Also: *Ann. Chim. et Phys.*, v. 5, 1895, pp. 289–405.

65. DEWAR, J., and J. A. FLEMING: Thermoelectric Powers of Metals and Alloys between the Temperatures of the Boiling Point of Water and the Boiling Point of Liquid Air, *Phil. Mag.*, v. 40, 1895, 95–119.

66. HICKS, W. M., and L. T. O'SHEA: Some Points Connected with the Preparation of Pure Iron by Electrolysis, *Electrician*, v. 35, 1895, pp. 843–844. Also: Univ. Sheffield Commemoration Volume, 1897.

67. ROBERTS-AUSTEN, W. C.: Third Report to the Alloys Research Committee, *Proc. Inst. Mech. Eng.*, 1895, pp. 238–253.

1896–1898

68. EWING, J. A.: The Magnetic Testing of Iron and Steel, *Proc. Inst. Civil Eng.*, v. 126, 1896, pp. 185–219.

69. FLEMING, J. A., and J. DEWAR: On the Magnetic Permeability and Hysteresis of Iron at Low Temperature, *Proc. Royal Soc.* (London), ser. A, v. 60, 1896, pp. 81–95.

70. HOLBORN, L., and W. WIEN: Die bisherigen Bestimmungen des Wärmeleitungsvermögens von Metallen (The Previous Determinations of the Thermal Conductivity of Metals), *Z. Ver. deutsch. Ing.*, v. 40, 1896, pp. 45–47.

71. LEICK, W.: Über das magnetische Verhalten galvanischer Eisen-, Nickel-, und Cobaltniederschläge (The Magnetic Properties of Electrolytic Iron, Nickel, and Cobalt), *Ann. d. Phys. u. Chem.*, new ser., v. 58, 1896, pp. 691–715; v. 59, 1896, pp. 750–752.

72. McGILLIVRAY, W. A.: The Preparation of Chemically Pure Iron, *Industries & Iron*, v. 21, 1896, pp. 69–70.

73. NICHOLSON, H. H., and S. AVERY: Notes on the Electrolytic Estimation of Iron, Nickel and Zinc, *J. Am. Chem. Soc.*, v. 18, 1896, pp. 654–659.

74. HOULLEVIGUE, M. L.: Étude expérimentale du fer électrolytique (Experimental Investigation of Electrolytic Iron), *J. de Physique*, v. 6, 1897, pp. 246–252.

75. MORRIS, D. K.: On the Magnetic Properties and Electrical Resistance of Iron as Dependent upon Temperature, *Phil. Mag.*, v. 44, 1897, pp. 213–254.

76. RICHARDS, J. W.: Relations between the Melting Points and the Latent Heats of Fusion of the Metals, *J. Franklin Inst.*, v. 143, 1897, pp. 379–383.

77. RUBENS, H., and E. F. NICHOLS: Versuche mit Wärmestrahlen von grosser Wellenlänge (Experiments with Heat Rays of Long Wave Lengths), *Ann. d. Phys. u. Chem.*, new ser., v. 60, 1897, pp. 418–462.

78. GOLDSCHMIDT, H.: Über ein neues Verfahren zur Darstellung von Metallen und Legierungen mittelst Aluminiums (A New Method for the Preparation of Metals and Alloys by Means of Aluminum), *Liebig's Ann. d. Chemie.*, v. 301, 1898, pp. 19–28. Also: *Z. f. Elektrochemie*, v. 4, 1898, p. 494–499.

79. HABER, F.: Über galvanisch gefälltes Eisen (Electrodeposited Iron), *Z. f. Elektrochemie*, v. 4, 1898, pp. 410–413.

80. LeCHATELIER, H.: Sur la résistance électrique des aciers (Electric Resistance of Steels), *C. R. Acad. Sci.*, Paris, v. 126, 1898, pp. 1709–1711; 1782–1785.

81. NAGAOKA, H., and K. HONDA: On Magnetostriction, *Phil. Mag.*, v. 46, 1898, pp. 261–290.

82. STEAD, J. E.: The Crystalline Structure of Iron and Steel, *J. Iron Steel Inst.*, v. 53, 1898, pp. 145–189.

83. TROWBRIDGE, A.: Über die Dispersion des Sylvins und das Reflexionsvermögen der Metalle (The Dispersion of Sylvite and the Reflecting Power of Metals), *Ann. d. Phys. u. Chem.*, new ser., v. 65, 1898, pp. 595–620.

84. WILSON, E.: The Magnetic Properties of almost Pure Iron, *Proc. Royal Soc.* (London), ser. A, v. 62, 1898, pp. 369–376.

1899–1900

85. AVERY, S., and B. DALES: Die Fehler-Quellen bei der elektrolytischen Bestimmung des Eisens (Sources of Error in the Electrolytic Determination of Iron), *Ber. Deutsch. Chem. Ges.*, v. 32, 1899, pp. 64–68.

86. AVERY, S., and B. DALES: Der Kohlenstoffgehalt des elektrolytisch ausgeschiedenen Eisens. Bemerkungen zu einem Aufsatz der HHrn Hans Verwer und Friedrich Groll (The Carbon Content of Electrolytic Iron. Discussion of a Paper by Verwer and Groll), *Ber. Deutsch. Chem. Ges.*, v. 32, 1899, pp. 2233–2238.

87. KAHLBAUM, G. W. A.: Über Metalldestillation (Metal Distillation), *Physik. Z.*, v. 1, 1899–1900, pp. 62–64; 67–69.

88. KORDA, D.: L'Influence du magnétisme sur la conductibilité calorifique du fer (The Influence of Magnetism on the Thermal Conduc-

tivity of Iron), *C. R. Acad. Sci.*, Paris, v. 128, 1899, pp. 418–420. Also: *J. de Physique*, v. 1, 1902, pp. 307–311.

89. MARTENS, A.: "Handbook of Testing Materials," translated by G. C. Henning, John Wiley and Sons, New York, 1899, v. 1, pp. 266–267.

90. ROBERTS-AUSTEN, SIR W. C.: Fifth Report to the Alloys Research Committee, *Proc. Inst. Mech. Eng.*, 1899, pp. 35–68.

91. STANSFIELD, A.: The Present Position of the Solution Theory of Carburized Iron, *J. Iron Steel Inst.*, v. 56, 1899, pp. 169–179.

92. EWING, J. A.: "Magnetic Induction in Iron and Other Metals," The Electrician Printing and Publishing Co., London, 3rd ed., 1900, 393 pp.

93. HALL, E. H.: Concerning Thermal Conductivity in Iron, *Phys. Rev.*, ser. 1, v. 10, 1900, pp. 277–310.

94. HEYN, E.: Eisen und Wasserstoff (Iron and Hydrogen), *Stahl u. Eisen*, v. 20, 1900, pp. 837–844.

95. NAGAOKA, H., and K. HONDA: On the Change of Volume and of Length in Iron, Steel and Nickel Ovoids by Magnetization, *Phil. Mag.*, v. 49, 1900, pp. 329–343.

96. OSMOND, F.: On the Crystallography of Iron, *Metallographist*, v. 3, 1900, pp. 181–219; 275–290.

97. RICHARDS, T. W., and G. P. BAXTER: A Revision of the Atomic Weight of Iron, *Proc. Am. Acad. Arts and Sci.*, v. 35, 1900, pp. 253–260.

98. SCHWEITZER, A.: "Über den Einfluss der Magnetisierung auf das Wärmeleitungsvermögen des Eisens" (The Influence of Magnetization on the Thermal Conductivity of Iron), *Dissertation* 61S, Zürich, 1900. Abst.: *Beiblätter Ann. d. Physik*, v. 25, 1901, pp. 466–468.

99. STEAD, J. E.: Iron and Phosphorus, *J. Iron Steel Inst.*, v. 58, 1900, pp. 60–144.

1901

100. BARRETT, W. F., W. BROWN, and R. A. HADFIELD: Researches on the Electrical Conductivity and Magnetic Properties of Upwards of One Hundred Different Alloys of Iron, *J. Inst. Electrical Eng.*, v. 31, 1901–1902, pp. 674–721.

101. COEHN, A., and K. DANNENBERG: Über kathodische Polarisation und Bildung von Legierungen (Cathodic Polarization and the Formation of Alloys), *Z. phys. Chem.*, v. 38, 1901, pp. 609–629.

102. GUMLICH, E., and E. SCHMIDT: Magnetische Untersuchungen an neueren Eisensorten (Magnetic Investigation of New Varieties of Iron), *Elektrotechnische Z.*, v. 22, 1901, pp. 691–698.

103. HICKS, W. M.: The Permeability of Iron Alloys, *Nature*, v. 65, 1901–1902, p. 558.

104. MAURAIN, C.: Propriétés des dépots électrolytiques de fer obtenus dans un champ magnétique (Properties of Electrolytic Iron Deposited in a Magnetic Field), *J. de Physique*, ser. 3, v. 10, 1901, pp. 123–135.

105. OSMOND, F., and G. CARTAUD: On the Crystallography of Iron, *Metallographist*, v. 4, 1901, pp. 119–149; 236–252.

106. VERWER, H.: Über die Bildung von Kohlenstoff bei der Elektrolyse von Ammoniumoxalatlösungen (The Formation of Carbon during Electrolysis of Solutions of Ammonium Oxalates), *Chemiker Z.*, v. 25, 1901, pp. 792–793.

1902

107. BENEDICKS, C.: Der elektrische Leitungswiderstand des Stahles und des reinen Eisens (The Electric Resistance of Steel and Pure Iron), *Z. phys. Chem.*, v. 40, 1902, pp. 545–558.

108. CHARPY, G., and L. GRENET: Sur la dilatation des aciers aux températures élevées (The Dilatation of Steel at Elevated Temperatures), *C. R. Acad. Sci.*, Paris, v. 134, 1902, pp. 540–542.

109. CHARPY, G., and L. GRENET: Étude des transformations des aciers par la méthode dilatométrique (Investigation of the Transformations of Steel by the Dilatometric Method), *C. R. Acad. Sci.*, Paris, v. 134, 1902, pp. 598–601.

110. HARRISON, E. P.: On the Variation with Temperature of the Thermoelectromotive Force and of the Electric Resistance of Nickel, Iron, and Copper between the Temperatures of −200°C. and +1050°, *Phil. Mag.*, v. 3, 1902, pp. 177–195.

111. NAGAOKA, H., and K. HONDA: On the Magnetostriction of Steel, Nickel, Cobalt and Nickel Steels, *Phil. Mag.*, v. 4, 1902, pp. 45–72.

112. SKRABAL, A.: Über Darstellung von reinem Eisen (Preparation of Pure Iron), *Ber. Deutsch. Chem. Ges.*, v. 35, 1902, pp. 3404–3405.

1903

113. BLYTH, V. J.: On the Influence of the Magnetic Field on Thermal Conductivity, *Phil. Mag.*, v. 5, 1903, pp. 529–537.

114. BURGESS, C. F.: A Practical Utilization of the Passive State of Iron, *Trans. Am. Electrochem. Soc.*, v. 4, 1903, pp. 31–36.

115. GULDBERG, C. M.: Thermodynamische Abhandlungen über Molekulartheorie und chemische Gleichgewichte (Thermodynamic Treatise on Molecular Theories and Chemical Equilibria), Ostwald's Klassiker der exakten Wissenschaften, No. 139, 1903, p. 24.

116. HONDA, K., and S. SHIMIZU: Change of Length of Ferromagnetic Substances under High and Low Temperatures by Magnetization, *Phil. Mag.*, v. 6, 1903, pp. 392–400.

117. LAFAY, A.: Sur la conductibilité calorifique du fer dans le champ magnétique (Thermal Conductivity of Iron in the Magnetic Field), *C. R. Acad. Sci.*, Paris, v. 136, 1903, pp. 1308–1310.

1904

118. BAUSENWEIN, E. G.: Änderung des Peltiereffektes mit der Temperatur (Change of Peltier Effect with Temperature), *Ann. d. Physik*, ser. 4, v. 15, 1904, pp. 213–224.

119. BENEDICKS, C.: "Recherches physiques et physico-chimiques sur l'acier au carbone" (Physical and Physicochemical Investigations of Carbon Steel), *Dissertation*, Upsala, 1904, 215 pp.

120. BURGESS, C. F., and C. HAMBUECHEN: Electrolytic Iron, *Trans. Am. Electrochem. Soc.*, v. 5, 1904, pp. 201–207.

121. CARPENTER, H. C. H., and B. F. E. KEELING: The Range of Solidification and the Critical Ranges of Iron-carbon Alloys, *J. Iron Steel Inst.*, v. 65, 1904, pp. 224–242.

122. DEWAR, SIR JAMES, and R. A. HADFIELD: The Effect of Liquid Air Temperatures on the Mechanical and Other Properties of Iron and Its Alloys, *Proc. Royal Soc.* (London), ser. A, v. 74, 1904–1905, pp. 326–336.

123. FRISBIE, F. C.: The Effect of Pressure on Magnetic Induction, *Phys. Rev.*, ser. 1, v. 18, 1904, pp. 432–443.

124. NEUBURGER, A.: Einige Bemerkungen zu dem Vortrag von Burgess und Hambuechen über "Elektrolytisches Eisen" (Discussion of the Work of Burgess and Hambuechen on Electrolytic Iron), *Elektrochemische Z.*, v. 11, 1904, pp. 77–78.

125. SKRABAL, A.: Über das Elektrolyteisen (Electrolytic Iron), *Z. f. Elektrochemie*, v. 10, 1904, pp. 749–752.

126. SKRABAL, A.: Zur Reindarstellung des Eisens als Titersubstanz für massanalytische Zwecke (Purification of Iron for a Standard for Volumetric Analysis), *Z. anal. Chem.*, v. 43, 1904, pp. 97–98.

127. ZAHN, H.: Über die galvanomagnetischen und thermomagnetischen Effekte in verschiedenen Metallen (The Galvanomagnetic and Thermomagnetic Effects in Different Metals), *Ann. d. Physik*, ser. 4, v. 14, 1904, pp. 886–935.

1905

128. BRAUNE, H.: Influence de l'azote sur le fer et l'acier (Influence of Nitrogen on Iron and Steel), *Rev. de Mét.*, *Mém.*, v. 2, 1905, pp. 498–502. Also: Über die Bedeutung des Stickstoffes im Eisen (The Significance of Nitrogen in Iron), *Stahl u. Eisen*, v. 26, 1906, pp. 1357–1363.

129. HADFIELD, R. A.: Experiments Relating to the Effect on Mechanical and other Properties of Iron and its Alloys Produced by Liquid Air Temperatures, *J. Iron Steel Inst.*, v. 67, 1905, pp. 147–255.

130. HALL, E. H., L. L. CAMPBELL, S. B. SERVISS, and E. P. CHURCHILL: On the Thomson Effect and Temperature Coefficient of Thermal Conductivity of Soft Iron, 115–204°C., *Proc. Am. Acad. Arts and Sci.*, v. 41, 1905–1906, pp. 21–55.

131. HARKER, J. A.: The Specific Heat of Iron at High Temperatures, *Phil. Mag.*, v. 10, 1905, pp. 430–438. Also: *Proc. Phys. Soc.* (London), v. 19, 1903–1905, pp. 703–712.

132. HONDA, K., and S. SHIMIZU: On the Magnetization and the Magnetic Change of Length in Ferromagnetic Metals and Alloys at Temperatures Ranging from −186°C. to 1200°C., *Phil. Mag.*, v. 10, 1905, pp. 548–574.

133. Maximowitsch, S.: Ein neues Verfahren zur Herstellung des Elektrolyteisens (A New Process for Making Electrolytic Iron), *Z. f. Elektrochemie*, v. 11, 1905, pp. 52–53.

134. Osmond, F., and C. Frémont: Les propriétés méchaniques du fer en cristaux isolés (The Mechanical Properties of Single Crystals of Iron), *C. R. Acad. Sci.*, Paris, v. 141, 1905, pp. 361–363.

135. Stanton, T. E., and L. Bairstow: On the Resistance of Iron and Steel to Reversals of Direct Stress, *Proc. Inst. Civil Eng.*, v. 166, 1905–1906, pp. 78–110.

136. Warburg, E.: "Die Tätigkeit der Physikalisch-Technischen Reichsanstalt im Jahre 1905" (Annual report of the Reichsanstalt for 1905), Julius Springer, Berlin, p. 191.

137. Williams, W. E.: On the Magnetic Change of Resistance in Iron, Nickel, and Nickel Steel at Various Temperatures, *Phil. Mag.*, v. 9, 1905, pp. 77–85.

138. Zahn, H.: Über die transversalen galvanomagnetischen und thermomagnetischen Effekte in verschiedenen Metallen (Transverse Galvanomagnetic and Thermomagnetic Effects in Different Metals), *Ann. d. Physik*, ser. 4, v. 16, 1905, pp. 148–154.

1906

139. Boynton, H. C.: Hardness of the Constituents of Iron and Steel, *J. Iron Steel Inst.*, v. 70, 1906, pp. 287–318.

140. Burgess, C. F., and S. G. Engle: Observations on the Corrosion of Iron by Acids, *Trans. Am. Electrochem. Soc.*, v. 9, 1906, pp. 199–206.

141. Burgess, C. F., and A. H. Taylor: Magnetic Properties of Electrolytic Iron, *Trans. Am. Inst. Elec. Eng.*, v. 25, 1906, pp. 459–465.

142. Burgess, C. F., and O. P. Watts: Structure of Electro-deposits, *Trans. Am. Electrochem. Soc.*, v. 9, 1906, pp. 229–237.

143. Charpy, G.: Sur l'influence de la température sur la fragilité des métaux (Influence of Temperature on the Brittleness of Metals), International Association for Testing Materials, *Congress Brussels*, 1906, A 17f, 9 pp.

144. Hall, E. H., L. L. Campbell, S. B. Serviss, and E. P. Churchill: On the Thomson Effect and the Temperature Coefficient of Thermal Conductivity in Soft Iron between 115° and 204°C., *Proc. Am. Acad. Arts and Sci.* v. 42, 1906–1907, pp. 597–626.

145. Lecher, E.: Thomsoneffekt in Eisen, Kupfer, Silber und Konstantan (Thomson Effect in Iron, Copper, Silver, and Constantan), *Ann. d. Physik*, ser. 4, v. 19, 1906, pp. 853–867; v. 20, 1906, pp. 480–502.

146. Onnes, H. K., and C. A. Crommelin: On the Measurement of Very Low Temperatures. IX. Comparison of a Thermoelement Constantin-steel with the Hydrogen Thermometer, Communications from Physical Lab. at the University of Leiden, v. 8, 1906, No. 95, pp. 2–24.

147. Osmond, F.: Les recherches de M. Fournel et la limite inférieure du point A_2 (Researches of Fournel and the Lower Limit of the A_2 point), *Rev. de Mét., Mém.*, v. 3, 1906, pp. 551–554.

148. Osmond, F., and G. Cartaud: The Crystallography of Iron, *J. Iron Steel Inst.*, v. 71, 1906, pp. 444–488.

149. Ryss, A., and A. Bogomolny: Studien über die elektrolytische Abscheidung des Eisens aus den wässerigen Lösungen seines Chlorürs und Sulfates (Electrolytic Deposition of Iron from Solutions of its Chloride and Sulphate), *Z. f. Elektrochemie*, v. 12, 1906, pp. 697–703.

150. Timmerman, J.: Les rapports de la dissociation des corps dissous et de leur réactivité (Relationship of the Dissociation of Dissolved Substances to Their Reactivity), *Bull. Soc. Chim. Belg.*, v. 20, 1906, pp. 305–313.

151. Treitschke, W., and G. Tammann: Über das Zustandsdiagramm von Eisen und Schwefel (The Equilibrium Diagram of Iron and Sulphur), *Z. anorg. Chem.*, v. 49, 1906, pp. 320–335.

152. Warburg, E.: "Die Tätigkeit der Physikalisch-Technischen Reichsanstalt im Jahre 1906" (Annual Report of the Reichsanstalt for 1906), Julius Springer, Berlin, p. 194.

1907

153. Burgess, G. K.: Melting Points of the Iron Group Elements by a New Radiation Method, *Bull. National Bur. of Stds.*, v. 3, 1907, 345–355.

154. Cermak, P.: Der Peltiereffekt Eisen-Konstantan und Nickel-Kupfer zwischen 0° und 560°C. (The Peltier Effect of Iron-constantan and Nickel-copper between 0° and 560°C.), *Ann. d. Physik*, ser. 4, v. 24, 1907, pp. 351–356.

155. Dorsey, H. G.: Coefficient of Linear Expansion at Low Temperatures, *Phys. Rev.*, v. 25, 1907, pp. 88–102.

156. Friedrich, K.: Eisen und Arsen (Iron and Arsenic), *Metallurgie*, v. 4, 1907, pp. 129–137.

157. Harkort, H.: Beitrag zum Studium des Systems Eisen-Wolfram (Contribution to the Study of the Iron-tungsten System), *Metallurgie*, v. 4, 1907, pp. 617–631; 639–647.

157A. Honda, K., and T. Terada: On the Effect of Stress on Magnetization and its Reciprocal Relations to the Change of Elastic Constants by Magnetization, *Phil. Mag.*, v. 14, 1907, pp. 65–115.

158. Isaac, E., and G. Tammann: Über das Verhalten von Eisen zu Blei, Wismut, Thallium und Cadmium (The Reaction of Iron with Lead, Bismuth, Thallium, and Cadmium), *Z. anorg. Chem.*, v. 55, 1907, pp. 58–62.

159. Isaac, E., and G. Tammann: Über die Legierungen des Eisens mit Platin (Alloys of Iron with Platinum), *Z. anorg. Chem.*, v. 55, 1907, pp. 63–71.

160. Isaac, E., and G. Tammann: Über die Legierungen des Eisens mit Zinn und Gold (Alloys of Iron with Tin and Gold), *Z. anorg. Chem.*, v. 53, 1907, p. 294.

161. Nordmeyer, P., and A. L. Bernoulli: Bestimmung der spezifischen Wärme einiger Elemente, Legierungen und Verbindungen zwischen

−185° and +20° (Determination of the Specific Heat of Some Elements, Alloys, and Compounds between −185 and +20°C.), *Verhand. Deutsch. Physik. Ges.*, v. 9, 1907, pp. 175–183.

162. OBERHOFFER, P.: Die spezifische Wärme des Eisens (The Specific Heat of Iron), *Metallurgie*, v. 4, 1907, pp. 427–443; 447–455; 486–497.

163. PERKIN, F. M., and L. PRATT: Reducing Action of Metallic Calcium and Calcium Hydride upon Metallic Oxides, Sulphides, and Halogen Salts, *Trans. Faraday Soc.*, v. 3, 1907, pp. 179–186.

164. PETRENKO, G. J.: Über die Legierungen des Silbers mit den Metallen der Eisengruppe (Alloys of Silver with the Metals of the Iron Group), *Z. anorg. Chem.*, v. 53, 1907, pp. 212–215.

165. RICHARDS, T. W., and F. N. BRINK: Linear Compressibility of Copper and Iron and the Cubic Compressibility of Mercury, Carnegie Inst., Washington, *Pub.* No. 76, 1907, pp. 43–52.

166. STROMEYER, C. E.: The Ageing of Mild Steel, *J. Iron Steel Inst.*, v. 73, 1907, pp. 200–254.

167. STROMEYER, C. E.: Further Experiments on the Ageing of Mild Steel, *J. Iron Steel Inst.*, v. 75, 1907, pp. 86–107.

168. WALKER, W. H., A. M. CEDERHOLM, and L. N. BENT: The Corrosion of Iron and Steel, *J. Am. Chem. Soc.*, v. 29, 1907, p. 1262.

169. WALKER, W. H., and C. DILL: The Effect of Stress upon the Electromotive Force of Soft Iron, *Trans. Am. Electrochem. Soc.*, v. 11, 1907, pp. 153–167.

170. WARBURG, E.: "Die Tätigkeit der Physikalisch-Technischen Reichsanstalt im Jahre 1907" (Annual Report of the Reichsanstalt for 1907), Julius Springer, Berlin, p. 184.

171. WEISS, P.: L'intensité d'aimantation à saturation du fer et du nickel (The Intensity of Magnetization at Saturation of Iron and Nickel), *C. R. Acad. Sci.*, Paris, v. 145, 1907, pp. 1155–1157.

1908

172. AMBERG, R.: Notiz zur Darstellung von Elektrolyteisen (Note on the Preparation of Electrolytic Iron), *Z. f. Elektrochemie*, v. 14, 1908, pp. 326–328.

173. BRISKER, C.: Die latente Schmelzwärme des reinen Eisens (The Latent Heat of Fusion of Pure Iron), *Metallurgie*, v. 5, 1908, pp. 183–184.

174. CARPENTER, H. C. H.: The Freezing Point of Iron, *J. Iron Steel Inst.*, v. 78, 1908, pp. 290–299.

175. COWPER-COLES, S. O.: The Production of Finished Iron Sheets and Tubes in One Operation, *J. Iron Steel Inst.*, v. 78, 1908, pp. 134–155.

176. GRÜNEISEN, E.: Die elastischen Konstanten der Metalle bei kleinen Deformationen. II. Torsionsmodul, Verhältnis von Querkontraktion zu Längsdilatation und kubische Kompressibilität (The Elastic Constants of Metals under Small Deformations. II. Torsion Modulus, Ratio of Transverse Contraction to Linear Expan-

sion, and Cubic Compressibility), *Ann. d. Physik*, ser. 4, v. 25, 1908, pp. 825–851.

177. GUMLICH, E.: Über die magnetischen Eigenschaften einer von Herrn Dr. Kreusler hergestellten Probe reinen Eisens (Magnetic Properties of a Specimen of Pure Iron Prepared by Dr. Kreusler), *Ver hand. Deutsch. Phys. Ges.*, v. 10, 1908, pp. 371–376.

178. GWYER, A. G. C.: Über die Legierungen des Aluminiums mit Kupfer, Eisen, Nickel, Kobalt, Blei und Cadmium (Alloys of Aluminum with Copper, Iron, Nickel, Cobalt, Lead, and Cadmium), *Z. anorg. Chem.*, v. 57, 1908, pp. 113–153.

179. KERN, E. F.: Electrolytic Refining of Iron, *Trans. Am. Electrochem. Soc.*, v. 13, 1908, pp. 103–119.

180. KREUSLER, H.: Über reines Eisen (Pure Iron), *Verhand. Deutsch. Phys. Ges.*, v. 10, 1908, pp. 344–350.

181. KURNAKOW, N. S., and N. S. KONSTANTINOW: Antimonide des Eisens und des Cadmiums (Antimonides of Iron and of Cadmium), *Z. anorg. Chem.*, v. 58, 1908, pp. 1–22.

182. NICCOLAI, G.: Über den elektrischen Widerstand der Metalle zwischen sehr hohen und sehr tiefen Temperaturen (The Electric Resistance of Metals between Very High and Very Low Temperatures), *Physik. Z.*, v. 9, 1908, pp. 367–372.

183. NORDMEYER, P.: Die spezifische Wärme einiger Elemente und Salze zwischen der Temperatur der flüssigen Luft und Zimmertemperatur (The Specific Heat of some Elements and Salts between the Temperature of Liquid Air and Room Temperature), *Verhand. Deutsch. Phys. Ges.*, v. 10, 1908, pp. 202–206.

183A. ONNES, H. K., and J. CLAY: On the Measurement of Very Low Temperatures. XXII. The Thermoelement Gold-silver at Liquid Hydrogen Temperatures, Communications from Physical Lab. at the University of Leiden, v. 9, 1908, No. 107, pp. 15–16.

184. SAKLATWALLA, B.: Constitution of Iron and Phosphorus Compounds, *J. Iron Steel Inst.*, v. 77, 1908, pp. 92–103.

185. SCHILD, K.: Die magnetischen Eigenschaften elektrolytischer Eisenniederschläge (The Magnetic Properties of Electrolytic Iron), *Ann. d. Physik*, ser. 4, v. 25, 1908, pp. 586–622.

186. WARBURG, E.: "Die Tätigkeit der Physikalisch-Technischen Reichsanstalt im Jahre 1908" (Annual Report of the Reichsanstalt for 1908), Julius Springer, Berlin, pp. 190–191.

187. WEISS, P., and P. N. BECK: Chaleur spécifique et champ moléculaire des substances ferromagnétiques (Specific Heat and Molecular Field of Ferromagnetic Materials), *Arch. Sci. Phys. et Naturelles*, v. 25, 1908, pp. 529–548. Also: *J. de Physique*, v. 7, 1908, pp. 249–264.

1909

188. ANON.: Die Langbein-Pfanhauser-Werke, Aktiengesellschaft, Leipzig S. (The Langbein-Pfanhauser Works at Leipzig), *Z. f. Elektrochemie*, v. 15, 1909, p. 595–596.

189. BAKER, T.: Gases Occluded in Steel, *Iron Steel Inst., Carn. Schol. Mem.*, v. 1, 1909, pp. 219–229; v. 3, 1911, pp. 249–259.

190. FOERSTER, F., with V. HEROLD, O. MUSTAD, and H. LEE: Beiträge zur Kenntnis des elektrochemischen Verhaltens des Eisens (The Electrochemical Properties of Iron), *Abhand. Deutsch. Bunsen Ges.*, No. 2, 1909, 83 pp. (59–81).

191. FRIEND, J. N.: The Action of Air and Steam on Pure Iron, *Engineering*, v. 88, 1909, pp. 526–527.

192. GREENWOOD, H. C.: An Approximate Determination of the Boiling Points of Metals, *Proc. Royal Soc.* (London), ser. A, v. 82, 1909, pp. 396–408.

193. GUILLET, L., and L. RÉVILLON: Expériences sur l'essai au choc à température variable (Impact Tests at Various Temperatures), *Rev. de Mét., Mém.*, v. 6, 1909, p. 96; v. 7, 1910, pp. 837–844.

194. GUMLICH, E.: Die Messung hoher Induktionen. Einige physikalische Eigenschaften von Eisen-Silicium-Legierungen (The Measurement of High Inductions. Some Physical Properties of Iron-silicon Alloys), *Z. f. Elektrochemie*, v. 15, 1909, pp. 597–599.

195. GUMLICH, E.: Über die Messung hoher Induktionen (Measurements of High Inductions), *Elektrotechnische Z.*, v. 30, 1909, pp. 1065–1067; 1096–1100.

196. MÜLLER, A.: Über die Darstellung des Elektrolyteisens, dessen Zusammensetzung und thermische Eigenschaften (The Preparation of Electrolytic Iron, Its Composition and Thermal Properties), *Metallurgie*, v. 6, 1909, pp. 145–160.

197. PATTEN, H. E., and W. H. MOTT: Electro-deposition of Some Metals from Acetone Solutions, *Trans. Am. Electrochem. Soc.*, v. 15, 1909, pp. 529–532.

198. PFAFF, A.: Über den Schwefelgehalt des Elektrolyteisens (The Sulphur Content of Electrolytic Iron), *Z. f. Elektrochemie*, v. 15, 1909, pp. 703–705.

199. PORTEVIN, A.: Contribution to the Study of the Special Ternary Steels, *Iron Steel Inst., Carn. Schol. Mem.*, v. 1, 1909, pp. 230–364.

200. STROMEYER, C. E.: The Ageing of Mild Steel and the Influence of Nitrogen, *J. Iron Steel Inst.*, v. 79, 1909, pp. 404–420.

201. WAGGONER, C. W.: The Effect of Low Temperature on Some of the Physical Properties of a Series of Iron-carbon Alloys, *Phys. Rev.*, ser. 1, v. 28, 1909, pp. 393–404.

202. WARBURG, E.: "Die Tätigkeit der Physikalisch-Technischen Reichsanstalt im Jahre 1909" (Annual Report of the Reichsanstalt for 1909), Julius Springer, Berlin, p. 190.

1910

203. AALDERINK, A.: Détermination de l'effet Thomson dans le fer à diverses températures (Determination of the Thomson Effect in Iron at Various Temperatures), *Arch. Néerlandaises des Sciences*, ser. 2, v. 15, 1910, pp. 321–352.

204. AMBERG, R.: Zur elektrolytischen Darstellung reinen Eisens (The Electrolytic Preparation of Pure Iron), *Z. f. Elektrochemie*, v. 16, 1910, pp. 125–129.

205. AUPPERLE, J. A.: The Attainment of Highest Purity Iron on a Commercial Basis, *Met. Chem. Eng.*, v. 8, 1910, pp. 262–265.

206. BECK, E.: Absolute Messungen über den Peltier-Effekt (Absolute Measurements of the Peltier Effect), *Vierteljahrsschrift der naturforschenden Ges.*, Zurich, v. 55, 1910, pp. 103–155; 470–482.

207. BERG, O.: Über den Thomsoneffekt in Kupfer, Eisen und Platin (The Thomson Effect in Copper, Iron, and Platinum), *Ann. d. Physik*, ser. 4, v. 32, 1910, pp. 477–519.

208. BURGESS, C. F., and J. ASTON: The Magnetic Properties of Electrolytic Iron and Some Commercial Steels, *Met. Chem. Eng.*, v. 8, 1910, pp. 191–194.

209. CUSHMAN, A. S., and H. A. GARDNER: "The Corrosion and Preservation of Iron and Steel," McGraw-Hill Book Company, Inc. New York, 1910, 373 pp.

210. DORSEY, H. G.: Magnetostriction in Iron-carbon Alloys, *Phys. Rev.*, ser. 1, v. 30, 1910, pp. 698–719.

211. FRIEDRICH, K.: Notiz über das Schmelzdiagramm des Systemes Schwefeleisen-Eisen (Note on the FeS-Fe Diagram), *Metallurgie*, v. 7, 1910, pp. 257–261.

212. GRÜNEISEN, E.: Einfluss der Temperatur auf die Kompressibilität der Metalle (Influence of Temperature on the Compressibility of Metals), *Ann. d. Physik*, ser. 4, v. 33, 1910, pp. 1239–1274.

213. HALL, E. H., and L. L. CAMPBELL: On the Electromagnetic and the Thermomagnetic Transverse and Longitudinal Effects in Soft Iron, *Proc. Am. Acad. Arts and Sci.*, v. 46, 1910–1911, pp. 625–658.

214. HEGG, F.: Étude thermomagnétique sur les ferro-nickels (A Thermomagnetic Study of Iron-nickel Alloys), *Arch. Sci. Phys. et Naturelles*, v. 30, 1910, p. 42.

215. KONSTANTINOW, N.: Über die Phosphide des Eisens (Iron Phosphides), *Z. anorg. Chem.*, v. 66, 1910, pp. 209–228.

216. LAMBERT, B., and J. C. THOMSON: The Wet Oxidation of Metals. Part I. The Rusting of Iron, *J. Chem. Soc.*, v. 97, 1910, pp. 2426–2433.

217. MOLBY, F. A.: Rotary Power of Quartz, Cinnabar and Nicotine at Low Temperatures, *Phys. Rev.*, ser. 1, v. 31, 1910, pp. 291–310.

218. MOND, L., H. HERTZ, and M. D. COWAP: Some New Metallic Carbonyls, *J. Chem. Soc.*, v. 97, 1910, pp. 798–810.

219. PFAFF, A.: Über die elektrolytische Abscheidung von Eisen (The Electrolytic Deposition of Iron), *Z. f. Elektrochemie*, v. 16, 1910, pp. 217–223.

220. ROBIN, F.: Resistance of Steels to Crushing at all Temperatures, *Iron Steel Inst., Carn. Schol. Mem.*, v. 2, 1910, pp. 70–270.

220A. ROSENHAIN, W., and J. C. W. HUMFREY: The Crystalline Structure of Iron at High Temperatures, *Proc. Royal Soc.* (London), ser. A, v. 83, 1910, pp. 200–209.

221. RUER, R., and E. SCHÜZ.: Das System Eisen-Nickel (The Iron-nickel System), *Metallurgie*, v. 7, 1910, pp. 415–420.

222. SCHLÖTTER, M.: "Galvanostegie," Part I, Wilhelm Knapp, Halle a. S., 1910, 257 pp.

223. SMITH, A. W.: The Variations of the Hall Effect in Metals with Change in Temperature, *Phys. Rev.*, ser. 1, v. 30, 1910, pp. 1–34.

224. SOMERVILLE, A. A.: Temperature Coefficients of Electrical Resistance, *Phys. Rev.*, ser. 1, v. 31, 1910, pp. 261–277.

225. TERRY, E. M.: The Effect of Temperature upon the Magnetic Properties of Electrolytic Iron, *Phys. Rev.*, ser. 1, v. 30, 1910, pp. 133–160.

226. TUCKER, S. A., and E. SCHRAMM: A Comparison of the Methods for Depositing Iron Electrolytically, *J. Ind. Eng. Chem.*, v. 2, 1910, pp. 237–239.

227. WEISS, P.: Mesure de l'intensité d'aimantation à saturation en valeur absolue (Measure of Intensity of Magnetization at Saturation in Absolute Values), *J. de Physique*, ser. 4, v. 9, 1910, pp. 373–393.

1911

228. BARKLA, C. G.: The Spectra of Fluorescent Röntgen Radiations, *Phil. Mag.*, v. 22, 1911, pp. 396–412.

229. BECKMAN, J. W.: An Electrolytic Furnace Method for Producing Metals, *Trans. Am. Electrochem. Soc.*, v. 19, 1911, pp. 171–175.

230. BURGESS, C. F.: Electrolytie Refining as a Step in the Production of Steel, *Trans. Am. Electrochem. Soc.*, v. 19, 1911, pp. 181–184.

231. CERMAK, P., and H. SCHMIDT: Die thermoelektrischen Kräfte beim Übergang vom festen zum flüssigen Aggregatzustande (Thermo-electric Forces at Transition from Solid to Liquid), *Ann. d. Physik*, ser. 4, v. 36, 1911, pp. 575–588.

232. COBB, J. W.: The Influence of Impurities on the Corrosion of Iron, *J. Iron Steel Inst.*, v. 83, 1911, pp. 170–190.

233. COBLENTZ, W. W.: The Reflecting Power of Various Metals, *Bull. National Bur. Stds.*, v. 7, 1911, pp. 197–225.

234. CUSHMAN, A. S.: The Manufacture of Pure Irons in Open-hearth Furnaces, *Proc. Am. Soc. Test. Mat.*, v. 11, 1911, pp. 387–408.

235. FRIEND, J. N.: "The Corrosion of Iron and Steel," Longmans, Green & Co., London, 1911, 300 pp.

236. FRIEND, J. N.: The Corrosion and Preservation of Iron, *Iron Steel Inst., Carn. Schol. Mem.*, v. 3, 1911, pp. 1–65.

237. FRIEND, J. N., and J. H. BROWN: The Action of Aqueous Solutions of Single and Mixed Electrolytes upon Iron, *J. Iron Steel Inst.*, v. 83, 1911, pp. 125–144.

238. FRIEND, J. N., and J. H. BROWN: Action of Salt Solutions and of Sea Water on Iron at Various Temperatures, *J. Chem. Soc.*, v. 99, 1911, pp. 1302–1306.

239. FRIEND, J. N., T. E. HULL, and J. H. BROWN: The Action of Steam on Iron at High Temperatures, *J. Chem. Soc.*, v. 99, 1911, pp. 969–973.

240. GOERENS, P.: On the Influence of Cold Working and Annealing on the Properties of Iron and Steel, *Iron Steel Inst., Carn. Schol. Mem.*, v. 3, 1911, pp. 320–434.

241. HEAPS, C. W.: The Effect of Magnetic Fields on Metallic Resistance, *Phil. Mag.*, v. 22, 1911, pp. 900–906.

242. HONDA, K., and H. TAKAGI: Über die Umwandlungen des Eisens und Stahles bei höheren Temperaturen (The Transformations of Iron and Steel at High Temperatures), *Sci. Rep.*. Sendai, ser. 1, v. 1, 1911–1912, pp. 207–217.

243. HONDA, K., and H. TAKAGI: Über die Suszeptibilität des Eisens, Stahles, Nickels und Kobalts bei höheren Temperaturen (The Susceptibility of Iron, Steel, Nickel, and Cobalt at High Temperatures), *Sci. Rep.*, Sendai, ser. 1, v. 1, 1911–1912, pp. 229–242.

244. KAUFMANN, W., and W. MEIER: Magnetische Eigenschaften elektrolytischer Eisenschichten (Magnetic Properties of Films of Electrolytic Iron), *Physik. Z.*, v. 12, 1911, pp. 513–522.

245. KOENIGSBERGER, J., and J. WEISS: Über die thermoelektrischen Effekte (Thermokräfte, Thomsonwärme) und die Wärmeleitung in einigen Elementen und die experimentelle Prüfung der Elektronentheorien (The Thermoelectric Effects—Thermoelectric Power, Thomson Heat—and the Thermal Conductivity of Several Elements and the Experimental Verification of the Electron Theory), *Ann. d. Physik*, ser. 4, v. 35, 1911, pp. 1–46.

246. MEYER, A. R.: Über die Änderung des elektrischen Widerstandes reinen Eisens mit Temperatur in dem Bereiche 0 bis 1000°C. (The Change of Electric Resistance of Pure Iron with Temperature from 0 to 1000°C.), *Verhand. Deutsch. Physik. Ges.*, v. 13, 1911, pp. 680–692.

247. RUFF, O.: Über das Zustandsdiagramm der Eisenkohlenstofflegierungen (Phase Diagram of Iron-carbon Alloys), *Metallurgie*, v. 8, 1911, pp. 456–464.

248. SIEVERTS, A.: Die Löslichkeit von Wasserstoff in Kupfer, Eisen und Nickel (The Solubility of Hydrogen in Copper, Iron, and Nickel), *Z. phys. Chem.*, v. 77, 1911, pp. 591–613.

249. STOFFEL, A.: Over de vorming van het ijzercarbonyl (The Production of Iron Carbonyl), *Chem. Weekblad*, v. 8, 1911, pp. 722–734.

250. WEISS, P., and G. FOËX: Étude de l'aimantation des corps ferromagnétiques au-dessus du point de Curie (Magnetization of Ferromagnetic Substances above the Curie Point), *J. de Physique*, ser. 5, v. 1, 1911, pp. 274–287.

1912

251. ALTERTHUM, H.: Über den Halleffekt in Metallen bei tiefen Temperaturen (The Hall Effect in Metals at Low Temperatures), *Ann. d. Physik*, ser. 4, v. 39, 1912, pp. 933–960.

252. ARNDT, K.: Zur Geschichte des Elektrolyteisens (A History of Electrolytic Iron), *Z. f. Elektrochemie*, v. 18, 1912, p. 233.

253. BAXTER, G. P., and C. R. HOOVER: A Revision of the Atomic Weight of Iron, *J. Am. Chem. Soc.*, v. 34, 1912, pp. 1657–1669.

254. BENEDICKS, C.: Allotropy of Iron and Silveriodide, Eighth Internat. Congress Appl. Chem., v. 22, 1912, pp. 13–27.

255. BENEDICKS, C.: On Allotropy in General and That of Iron in Particular, *J. Iron Steel Inst.*, v. 86, 1912, pp. 242–274.

256. DUISBERG, C.: Fortschritte und Probleme der chemischen Industrie (Achievements and Problems of the Chemical Industry), Eighth Internat. Congress Appl. Chem., v. 28, 1912, pp. 50–85.

257. GREENWOOD, H. C.: Über die Siedepunkte von Metallen (The Boiling Points of Metals), *Z. f. Elektrochemie*, v. 18, 1912, pp. 319–326.

258. GUMLICH, E.: Magnetische Eigenschaften von Eisen-Kohlenstoff- und Eisen-Siliciumlegierungen (Magnetic Properties of Iron-carbon and Iron-silicon Alloys), *Ferrum*, v. 10, 1912–1913, pp. 33–34. Also: *Trans. Faraday Soc.*, v. 8, 1912, pp. 98–114

259. HADFIELD, SIR ROBERT: Sinhalese Iron and Steel of Ancient Origin, *J. Iron Steel Inst.*, v. 85, 1912, pp. 134–172.

260. LAMBERT, B.: The Wet Oxidation of Metals. Part II, *J. Chem. Soc.*, v. 101, 1912, pp. 2056–2075; Part IV, *ibid.*, v. 107, 1915, pp. 218–222.

261. LOEBE, R., and E. BECKER: Das System Eisen-Schwefeleisen (The System Fe-FeS), *Z. anorg. Chem.*, v. 77, 1912, pp. 301–319.

262. MEUTHEN, A.: Kalorimetrische Untersuchung des Systems Eisen-Kohlenstoff (Calorimetric Investigation of the Iron-carbon System), *Ferrum*, v. 10, 1912–1913, pp. 1–21.

263. OOSTERHUIS, E.: Sur l'effet Peltier et le couple thermoélectrique fer-mercure (On the Peltier Effect and the Iron-mercury Thermocouple), *Arch. Néerlandaises des Sciences*, ser. 3A, v. 2, 1912, pp. 7–38.

264. ROBIN, F.: "Traité de Métallographie," A. Hermann et fils, Paris, 1912, p. 169.

265. SAUVEUR, A.: Note on the Crystalline Growth of Ferrite below its Thermal Critical Range, *Proc. Int. Assoc. Test. Mat.*, 6th Cong., New York, v. 2 (2), 1912, 12 pp.

266. SCHWARTZ, A.: Elektrische Temperaturmessung und Fernablesung unter besonderer Berücksichtigung des thermoelektrischen Verfahrens (Electric Measurement and Remote Reading of Temperatures with Special Reference to the Thermoelectric Method), *Z. Ver. deutsch. Ing.*, v. 56, 1912, pp. 223–229.

267. WATTS, O. P.: The Effect of Various Substances on the Rate of Corrosion of Iron by Sulphuric Acid, *Trans. Am. Electrochem. Soc.*, v. 21, 1912, pp. 337–353.

1913

268. BIDWELL, C. C.: Radiation from Solid and Molten Iron, *Phys. Rev.*, v. 1, 1913, pp. 482–483.

269. BORNEMANN, K., and K. WAGENMANN: Die elektrische Leitfähigkeit der Metallegierungen im flüssigen Zustande (The Electric Conduc-

tivity of Alloys in the Molten State), *Ferrum*, v. 11, 1913–1914, pp. 276–282; 289–320; 330–343.

270. BRESLAUER, M.: Die Verwendung des Elektrolyteisens im Elektromaschinenbau (The Use of Electrolytic Iron in the Construction of Electric Machinery), *Elektrotechnische Z.*, v. 34, 1913, pp. 671–674; 705–707.

271. BRONIEWSKI, W.: Sur les points critiques du fer (The Critical Points of Iron), *C. R. Acad. Sci.*, Paris, v. 156, 1913, pp. 699–702.

272. BRONIEWSKI, W.: Sur la thermo-électricité des aciers (The Thermo-electric Properties of Steels), *C. R. Acad. Sci.*, Paris, v. 156, 1913, pp. 1983–1985.

273. BUCK, D. M.: Copper in Steel—Its Influence on Corrosion, *Iron Age*, v. 91, 1913, pp. 931–936.

274. BURGESS, C. F., and J. ASTON: Influence of Various Elements on the Corrodibility of Iron, *J. Ind. Eng. Chem.*, v. 5, 1913, pp. 458–462.

275. BURGESS, G. K., and J. J. CROWE: The Critical Ranges A_2 and A_3 of Pure Iron, *Bull. Am. Inst. Min. Eng.*, 1913, pp. 2537–2591. Also: *National Bur. Stds. Sci. Papers*, v. 10, 1914, pp. 316–368.

276. CARPENTER, H. C. H.: The Critical Ranges of Pure Iron with Special Reference to the A_2 Inversion, *J. Iron Steel Inst.*, v. 87, 1913, pp. 315–326.

277. DANNECKER, C.: Über doppelte neutrale Punkte und die elektromotorischen Kräfte einiger Thermoelemente zwischen −200° und +1000°C. (Double Neutral Points and Electromotive Force of Thermoelements between −200° and +1000°C.), *Ann. d. Physik*, ser. 4, v. 42, 1913, pp. 1504–1530.

278. DEWAR, J.: Atomic Specific Heats between the Boiling Points of Liquid Nitrogen and Hydrogen, *Proc. Royal Soc.* (London), ser. A, v. 89, 1913–1914, pp. 158–169.

279. DRIESEN, J.: Untersuchungen über die thermische Ausdehnung und die Lösungsgeschwindigkeit von Kohlenstoffstählen (Investigation of the Thermal Expansion and the Rate of Solution of Carbon Steels), *Ferrum*, v. 11, 1913–1914, pp. 129–138; 161–169.

280. GOERENS, P., and G. HARTEL: Über die Zähigkeit des Eisens bei verschiedenen Temperaturen (The Toughness of Iron at Different Temperatures), *Z. anorg. Chem.*, v. 81, 1913, pp. 130–144.

281. GRIFFITHS, E. H., and E. GRIFFITHS: The Capacity for Heat of Metals at Different Temperatures, *Proc. Royal Soc.* (London), ser. A, v. 88, 1913, pp. 549–560. Also: *Phil. Trans. Royal Soc.* (London), v. 214, 1914, pp. 319–357.

282. GUILLET, L., and A. PORTEVIN: Sur quelques propriétés d'un fer électrolytique industriel (Some Properties of an Industrial Electrolytic Iron), *C. R. Acad. Sci.*, Paris, v. 156, 1913, pp. 702–705.

283. HANDY, J. O.: Production of Spongy Iron in Sweden, *Trans. Eng. Soc. of West. Pennsylvania*, v. 29, 1913–1914, pp. 29–30.

283A. HONDA, K.: Über die Wärmeerscheinungen und Magnetisierungsänderungen ferromagnetischer Körper bei höheren Temperaturen (Thermal Effects and Magnetic Changes in Ferromagnetic Sub-

stances at High Temperatures), *Sci. Rep.*, Sendai, ser. 1, v. 2, 1913, pp. 69–94.

284. LAMBERT, B.: An Electrolytic Theory of the Corrosion of Iron, *Trans. Faraday Soc.*, v. 9, 1913, pp. 108–114.

285. LAMONT, J.: Über Titaneisenlegierungen (Titanium-iron Alloys), *Ferrum*, v. 11, 1913–1914, pp. 225–234.

286. LEVIN, M., and K. DORNHECKER: Über das spezifische Volumen und über die Härte von Eisen-Kohlenstofflegierungen (The Specific Volume and Hardness of Iron-carbon Alloys), *Ferrum*, v. 11, 1913–1914, pp. 321–329.

287. McCULLOM, B., and K. H. LOGAN: Electrolytic Corrosion of Iron in Soils, *National Bur. Std. Tech. Papers* No. 25, 1913, 69 pp.

288. PALMAER, W., and J. A. BRINELL: Electrolytic Production of Iron Sheets and Tubes, *Met. Chem. Eng.*, v. 11, 1913, pp. 197–203.

289. RAYDT, U., and G. TAMMANN: Struktur und Eigenschaften von unter Druck zusammengeschmolzenen Zink-Eisenlegierungen (The Structure and Properties of Zinc-iron Alloys Melted under Pressure), *Z. anorg. Chem.*, v. 83, 1913, pp. 257–266.

290. ROBIN, F.: Recherches sur le développement des grains des métaux par recuit après écrouissage (Investigation on the Development of Grains in Metals by Annealing after Deformation), *Rev. de Mét., Mém.*, v. 10, 1913, pp. 722–768.

291. RUER, R., and K. FICK: Das System Eisen-Kupfer (The Iron-copper System), *Ferrum*, v. 11, 1913–1914, pp. 39–51.

292. RUER, R., and K. KANEKO: Das System Eisen-Kobalt (The Iron-cobalt System), *Ferrum*, v. 11, 1913–1914, pp. 33–39.

293. RUER, R., and R. KLESPER: Die γ-δ Umwandlung des reinen Eisens und ihre Beeinflussung durch Kohlenstoff, Silizium, Kobalt und Kupfer (The Gamma-delta Transformation in Pure Iron and the Influence of Carbon, Silicon, Cobalt, and Copper), *Ferrum*, v. 11, 1913–1914, pp. 257–261.

294. SAUVEUR, A.: The Allotropic Transformations of Iron, *J. Iron Steel Inst.*, v. 88, 1913, pp. 171–181.

295. STEAD, J. E., and H. C. H. CARPENTER: The Crystallizing Properties of Electrodeposited Iron, *J. Iron Steel Inst.*, v. 88, 1913, pp. 119–145.

296. UNWIN, F.: On the Hall and the Transverse Thermomagnetic Effects and Their Temperature Coefficients, *Proc. Royal Soc.* (Edinburgh), v. 34, 1913–1914, pp. 208–222.

1914

297. BENEDICKS, C.: Experiments on Allotropy of Iron: Behavior of Ferromagnetic Mixtures; Dilatation of Pure Iron, *J. Iron Steel Inst.*, v. 89, 1914, pp. 407–443.

298. BIDWELL, C. C.: A Comparison of Actual and Black Body Temperatures, *Phys. Rev.*, v. 3, 1914, pp. 439–449.

299. BRAGG, W. H., and S. E. PIERCE: The Absorption Coefficients of X-rays, *Phil. Mag.*, v. 28, 1914, pp. 626–630.

300. BURGESS, G. K., and R. G. WALTENBERG: Melting Points of the Refractory Elements. I. Elements of Atomic Weight from 48 to 59, *Bull. National Bur. Stds.*, v. 10, 1914, pp. 79–90.

301. CHAPPELL, C.: The Recrystallization of Deformed Iron, *J. Iron Steel Inst.*, v. 89, 1914, pp. 460–498.

302. FRIEND, J. N., and C. W. MARSHALL: The Influence of Molybdenum upon the Corrodibility of Steel, *J. Iron Steel Inst.*, v. 89, 1914, pp. 503–507.

303. GOTTSTEIN, G.: Über die Gültigkeit der thermodynamischen Beziehungen für Peltierwärme und Thomsonwärme und über die galvano- und thermomagnetischen Effekte bei variablen Leitern (The Validity of the Thermodynamic Relations of Peltier Heat and Thomson Heat and the Galvanomagnetic and Thermomagnetic Effects with Various Conductors), *Ann. d. Physik*, ser. 4, v. 43, 1914, pp. 1079–1100.

304. GUILLET, L.: Electrolytic Iron, Its Manufacture, Properties and Uses, *J. Iron Steel Inst.*, v. 90, 1914, pp. 66–80. Also: *Rev. de Mét., Mém.*, v. 12, 1915, pp. 81–94.

305. HEISING, R. A.: Magnetic Resistance Change of Pure Iron, *Phys. Rev.*, v. 4, 1914, pp. 315–324.

306. HONDA, K., and Y. OGURA: Über die Beziehung zwischen den Änderungen der Magnetisierung und des elektrischen Widerstandes im Eisen, Stahl und Nickel bei hohen Temperaturen (Relation between the Change of Magnetic Susceptibility and Electric Resistance of Iron, Steel and Nickel at Elevated Temperatures), *Sci. Rep.*, Sendai, ser. 1, v. 3, 1914, pp. 113–125.

307. KREMANN, R., and J. LORBER: Über die kathodischen funkenden Abscheidungen aus gemischten eisensulfat-magnesiumchlorid-glycerinhaltigen Bädern (Pyrophoric, Cathodic Deposits from Mixed Iron Sulphate, Magnesium Chloride, Glycerine Baths), *Monatsh. f. Chemie*, v. 35, 1914, pp. 1387–1422.

308. LASCHTSCHENKO, P. N.: Heats of Cooling of Aluminum, Iron, Antimony and Nickel, *J. Russ. Phys. Chem. Soc.*, v. 46, 1914, pp. 311–333. Abst.: *Chem. Absts.*, v. 8, 1914, pp. 2647–2648.

309. ONNES, H. K., and G. HOLST: Further Experiments with Liquid Helium M. (Preliminary Determination of the Specific Heat and of Thermal Conductivity of Mercury at Temperatures Obtainable with Liquid Helium, besides Some Measurements of Thermoelectric Forces and Resistances for the Purpose of Those Investigations), *Proc. K. Akad. Weten.*, Amsterdam, v. 17 (1), 1914, pp. 760–767.

310. PORTEVIN, A.: Sur la vitesse de transformation des aciers à l'échauffement et sur la résistance électrique spécifique du fer (The Velocity of Transformation of Steels on Heating and the Specific Electric Resistance of Iron), *C. R. Acad. Sci.*, Paris, v. 159, 1914, pp. 51–53.

311. RUER, R., and K. KANEKO: Über eine bei konstanter Temperatur verlaufende, mit starker Wärmetönung und starker Änderung der Magnetisierbarkeit verknüpfte polymorphe Umwandlung (On a

Polymorphic Constant-temperature Transformation Accompanied by a Pronounced Heat Effect and a Pronounced Change in Magnetizability), *Physik. Z.*, v. 15, 1914, pp. 17–18.

312. RUFF, O., and W. BORMANN: Arbeiten im Gebiete hoher Temperaturen. VII. Eisen und Kohlenstoff (Investigations at High Temperatures. VII. Iron and Carbon), *Z. anorg. Chem.*, v. 88, 1914, pp. 397–409.

313. RÜMELIN, G., and K. FICK: Beiträge zur Kenntnis des Systems Eisen-Mangan (The Iron-manganese System), *Ferrum*, v. 12, 1914–1915, pp. 41–44.

314. SAUVEUR, A.: Notes on Some Heating and Cooling Curves of Professor Carpenter's Electrolytic Iron, *Bull. Am. Inst. Min. Eng.*, 1914, pp. 255–257.

315. SCHIMANK, H.: Über das Verhalten des elektrischen Widerstands von Metallen bei tiefen Temperaturen (Electric Resistance of Metals at Low Temperatures), *Ann. d. Physik*, ser. 4, v. 45, 1914, pp. 706–736.

316. STOFFEL, A.: Über die Reaktion zwischen Kohlenoxyd und Eisen (The Reaction between Carbon Monoxide and Iron), *Z. anorg. Chem.*, v. 84, 1914, pp. 56–76.

317. STOREY, O. W.: A Microscopic Study of Electrolytic Iron, *Trans. Am. Electrochem. Soc.*, v. 25, 1914, pp. 489–527.

318. STRAUSS, B.: Mikroskopische Stahluntersuchung (Microscopic Examination of Steel), *Stahl u. Eisen*, v. 34, 1914, pp. 1814–1820.

319. WATTS, O. P., and M. H. Li: The Effect of Addition Agents in the Electrodeposition of Iron, *Trans. Am. Electrochem. Soc.*, v. 25, 1914, pp. 529–536.

320. WIETZEL, G.: Das thermoelektrische Verhalten der Metalle bei tiefen Temperaturen (The Thermoelectric Properties of Metals at Low Temperatures), *Ann. d. Physik*, ser. 4, v. 43, 1914, pp. 605–622.

321. YENSEN, T. D.: Magnetic and Other Properties of Electrolytic Iron Melted in Vacuo, Univ. Illinois Exp. Sta., *Bull.* 72, 1914, 71 pp.

1915

322. AITCHISON, L.: Experiments on the Corrosion of Molybdenum Steel, *J. Chem. Soc.*, v. 107, 1915, pp. 1531–1538.

323. AITCHISON, L.: Experiments on the Influence of Composition on the Corrosion of Steel, *Trans. Faraday Soc.*, v. 11, 1915, pp. 212–234.

324. AUSTIN, W.: The Influence of Oxygen on Some Properties of Pure Iron, *J. Iron Steel Inst.*, v. 92, 1915, pp. 157–161.

325. BECKMAN, B.: Über den Einfluss von Druck auf die elektrische Leitfähigkeit der reinen Metalle nach einer Theorie von E. Grüneisen (The Influence of Pressure on the Electric Conductivity of Pure Metals According to a Theory of E. Grüneisen), *Physik. Z.*, v. 16, 1915, pp. 59–62.

326. BURGESS, G. K., and I. N. KELLBERG: The Electrical Resistance and Critical Ranges of Pure Iron, *Bull. National Bur. Stds.*, v. 11, 1915, pp. 457–470.

327. BURGESS, G. K., and R. G. WALTENBERG: The Emissivity of Metals and Oxides. II. Measurements with the Micropyrometer, *Bull. National Bur. Stds.*, v. 11, 1915, pp. 591–605.

328. DUPUY, E. L., and A. PORTEVIN: The Thermoelectric Properties of Special Steels, *J. Iron Steel Inst.*, v. 91, 1915, pp. 306–335.

329. FREY, W.: Die Abhängigkeit des Halleffekts in Metallen von der Temperatur (The Effect of Temperature on the Hall Effect in Metals), *Ann. d. Physik*, ser. 4, v. 46, 1915, pp. 1057–1094.

330. FRIEND, J. N.: The Relative Corrodibilities of Iron and Steel, *Trans. Faraday Soc.*, v. 11, 1915, pp. 204–211.

330*A*. HONDA, K.: On the Nature of the A_2 Transformation in Iron, *J. Iron Steel Inst.*, v. 91, 1915, pp. 199–241.

331. HONDA, K., and H. TAKAGI: On a Magnetic Study of the A_3 Transformation in Pure Iron, *Sci. Rep.*, Sendai, ser. 1, v. 4, 1915, pp. 261–269. Also: *J. Iron Steel Inst.*, v. 92, 1915, pp. 190–195.

332. POMP, A.: Einfluss der Wärmebehandlung auf die Kerbzähigkeit, Korngrösse und Härte von kohlenstoffarmem Flusseisen (The Influence of Heat Treatment on Notch Toughness, Grain Size, and Hardness of Low-carbon Ingot Iron), *Ferrum*, v. 13, 1915–1916, pp. 49–59.

333. REINHOLD, O.: Über mechanische Eigenschaften von Flusseisen bei verschiedenen Temperaturen (The Mechanical Properties of Ingot Iron at Different Temperatures), *Ferrum*, v. 13, 1915–1916, pp. 97–103.

334. RICHARDS, T. W.: Concerning the Compressibilities of the Elements and Their Relations to Other Properties, *J. Am. Chem. Soc.*, v. 37, 1915, pp. 1643–1656.

335. ROSENHAIN, W.: Discussion of Note on Corrosion of Iron and Steel by S. Whyte, *Trans. Faraday Soc.*, v. 11, 1915, p. 237.

336. RUER, R., and F. GOERENS: Über die polymorphen Umwandlungen des reinen Eisens (The Polymorphic Transformations of Pure Iron), *Ferrum*, v. 13, 1915–1916, pp. 1–6.

337. RÜMELIN, G., and K. FICK: Beiträge zur Kenntnis des Systems Eisen-Mangan (The Iron-manganese System), *Ferrum*, v. 12, 1915, pp. 41–44.

338. SMITH, A. W., and A. W. SMITH: The Leduc Effect in Some Metals and Alloys, *Phys. Rev.*, v. 5, 1915, pp. 35–42.

339. SONÉ, T.: Magnetic Properties of Electrolytic Iron Deposited in Magnetic Fields, *Sci. Rep.*, Sendai, ser. 1, v. 4, 1915, pp. 313–321.

340. WILLIAMS, E. H.: Saturation Value of the Intensity of Magnetization and the Theory of the Hysteresis Loop, *Phys. Rev.*, v. 6, 1915, pp. 404–409.

341. YENSEN, T. D.: The Magnetic Properties of Some Iron Alloys Melted in Vacuo, *Trans. Am. Inst. Elec. Eng.*, v. 34, 1915, pp. 2601–2641.

342. YENSEN, T. D.: Magnetic and Other Properties of Iron-silicon Alloys, Melted in Vacuo, Univ. Illinois Exp. Sta., *Bull.* 83, 1915, 67 pp.

1916

343. AITCHISON, L.: The Theory of Corrosion of Steel, *J. Iron Steel Inst.*, v. 93, 1916, pp. 77–91.

344. ANON.: Le progrès de la fabrication du fer électrolytique (Progress in the Manufacture of Electrolytic Iron), *Lumière Électrique*, v. 35, 1916, p. 241.

345. ASTON, J.: The Effect of Rust upon the Corrosion of Iron and Steel, *Trans. Am. Electrochem. Soc.*, v. 29, 1916, pp. 449–464.

346. BENEDICKS, C.: A New Thermo-electric Method of Studying Allotropic Changes in Iron or Other Metals, *J. Iron Steel Inst.*, v. 93, 1916, pp. 211–220.

347. BRIDGMAN, P. W.: The Electrical Resistance of Metals under Pressure, *Proc. Am. Acad. Arts and Sci.*, v. 52, 1916–1917, pp. 571–646.

348. BURGESS, G. K., and H. SCOTT: Thermo-electric Measurement of the Critical Ranges of Pure Iron, *J. Iron Steel Inst.*, v. 94, 1916, pp. 259–267. Also: *Bull. National Bur. Stds.*, v. 14, 1918–1919, pp. 15–21.

349. CAIN, J. R., E. SCHRAMM, and H. E. CLEAVES: Preparation of Pure Iron and Iron-carbon Alloys, *Bull. National Bur. Stds.*, v. 13, 1916–1917, pp. 1–26. Also: *J. Ind. Eng. Chem.*, v. 8, 1916, pp. 217–224.

350. CAMPBELL, E. D.: The Influence of Heat Treatment on the Thermo-electric Properties and the Specific Resistance of Carbon Steels, *J. Iron Steel Inst.*, v. 94, 1916, pp. 268–285.

351. GÜNTHER, P.: Untersuchungen über die spezifische Wärme bei tiefen Temperaturen (Investigation of Specific Heat at Low Temperatures), *Ann. d. Physik*, ser. 4, v. 51, 1916, pp. 828–846.

352. HADFIELD, SIR R., and J. N. FRIEND: The Influence of Carbon and Manganese upon the Corrosion of Iron and Steel, *J. Iron Steel Inst.*, v. 93, 1916, pp. 48–70.

353. OESTERHELD, G.: Über die Legierungen des Berylliums mit Aluminium, Kupfer, Silber und Eisen (Alloys of Beryllium with Aluminum, Copper, Silver, and Iron), *Z. anorg. allgem. Chem.*, v. 97, 1916, pp. 6–40.

354. RUER, R., and F. GOERENS: Das System Eisen-Kupfer (The Iron-copper System), *Ferrum*, v. 14, 1916–1917, pp. 49–61.

355. SALDAU, P.: Apparatus for the Measurement of Electric Resistance of Material in the Solid State at High Temperatures, and Its Application to the Determination of the Critical Points of Iron and Steel, *Iron Steel Inst., Carn. Schol. Mem.*, v. 7, 1916, pp. 195–231.

356. STEAD, J. E.: Discussion of paper by L. Aitchison, The Theory of Corrosion of Steel, *J. Iron Steel Inst.*, v. 93, 1916, p. 99.

357. STOREY, O. W.: Review of Recent Progress in Electrolytic Iron, *Trans. Am. Electrochem. Soc.*, v. 29, 1916, pp. 357–367. Also: *Met. Chem. Eng.*, v. 14, 1916, pp. 534–536.

358. THOMPSON, F. C.: The Electrical and Magnetic Properties of Pure Iron in Relation to the Crystal Size, *Phil. Mag.*, v. 31, 1916, pp. 357–366.

359. WEISS, P., A. PICCARD, and A. CARRARD: Calorimétrie des substances ferro-magnétiques (Calorimetry of Ferro-magnetic. Materials), *Arch. Sci. Phys. et Naturelles*, v. 42, 1916, pp. 378–401; v. 43, 1917, pp. 27–52; 113–130; 199–216.

360. YENSEN, T. D.: The Effect of Vacuum Fusion upon the Magnetic Properties of Pure Open Hearth Iron, *Met. Chem. Eng.*, v. 14, 1916, pp. 585–586.

1917

361. ARCHIBALD, E. H., and L. A. PIGUET: The Electrolytic Deposition of Iron from Organic Solvents, *Trans. Royal Soc. Canada*, ser. 3, v. 11, 1917–1918, pp. 107–112.

362. BENNETT, C. W., and W. S. BURNHAM: The Passive State of Metals, *J. Phys. Chem.*, v. 21, 1917, pp. 107–149.

363. BORELIUS, G.: Eine Methode für kombinierte Messung von Peltier-wärme und Wärmeleitfähigkeit (A Method for the Combined Measurement of Peltier Heat and Thermal Conductivity), *Ann. d. Physik*, ser. 4, v. 52, 1917, pp. 398–414.

364. BRIDGMAN, P. W.: Thermo-electromotive Force, Peltier Heat and Thomson Heat under Pressure, *Proc. Am. Acad. Arts and Sci.*, v. 53, 1917–1918, pp. 269–386.

365. CAMPBELL, E. D.: Influence of Temperature of Measurement on the Electrical Resistivity and Thermo-electromotive Potential of Solutes in Steels, *Trans. Am. Electrochem. Soc.*, v. 32, 1917, pp. 193–208.

366. CHEVENARD, P.: Dilatomètre Différentiel Enregistreur (Recording Differential Dilatometer), *Rev. de Mét.*, *Mém.*, v. 14, 1917, pp. 610–640.

367. COMSTOCK, G. F.: A Method for Distinguishing Sulphides from Oxides in the Metallography of Steel, *Trans. Am. Inst. Min. Eng.*, v. 56, 1917, pp. 553–560.

368. DURRER, R.: Eine thermoelektrische Methode für das Studium der allotropen Umwandlungen der Metalle (A Thermoelectric Method for Studying Allotropic Changes in Metals), *Stahl u. Eisen*, v. 37, 1917, pp. 430–431.

369. GHOSH, J. C.: The Discharge Potential of Ions on Heated Electrodes, *J. Phys. Chem.*, v. 21, 1917, pp. 426–432.

370. HONDA, K.: On the Thermal Expansion of Different Kinds of Steel at High Temperatures, *Sci. Rep.*, Sendai, ser. 1, v. 6, 1917–1918, pp. 203–212.

371. HONDA, K., and T. MURAKAMI: On the Structure of Tungsten Steel and Its Change under Heat Treatment, *Sci. Rep.*, Sendai, ser. 1, v. 6, 1917–1918, pp. 235–283.

372. HONDA, K., and T. SIMIDU: On the Thermal and Electrical Conductivities of Carbon Steels at High Temperatures, *Sci. Rep.*, Sendai, ser. 1, v. 6, 1917–1918, pp. 219–233.

373. HOWE, H. M.: On Grain Growth, *Trans. Am. Inst. Min. Eng.*, v. 56, 1917, pp. 582–588.

374. HULL, A. W.: The Crystal Structure of Iron, *Phys. Rev.*, v. 9, 1917, pp. 84–87.

375. HULL, A. W.: A New Method of X-ray Crystal Analysis, *Phys. Rev.*, v. 10, 1917, pp. 661–696.

376. ISHINO, M.: The Scattering and the Absorption of the Gamma Rays, *Phil. Mag.*, v. 33, 1917, pp. 129–146.

377. ISHIWARA, T.: On the Magnetic Investigation of A_3 and A_4 Transformations in Pure Iron and Steels, *Sci. Rep.*, Sendai, ser. 1, v. 6, 1917–1918, pp. 133–138.

378. JEFFRIES, Z.: The Amorphous Metal Hypothesis and Equicohesive Temperatures, *J. Am. Inst. Metals*, v. 11, 1917, pp. 300–323.

379. JEFFRIES, Z.: Grain Growth Phenomena in Metals, *Trans. Am. Inst. Min. Eng.*, v. 56, 1917, pp. 571–581.

380. KOWALKE, O. L.: Acid Resisting Properties of Some Iron-silicon Alloys, *Trans. Am. Electrochem. Soc.*, v. 31, 1917, pp. 205–210.

381. KREMANN, R., and H. BREYMESSER: Über die bei gewöhnlicher Temperatur unter höheren Wasserstoffdrucken erhaltenen kathodischen Abscheidungen von Eisen und Eisen-Nickellegierungen (Cathodic Deposits of Iron and Iron-nickel Alloys Obtained at Ordinary Temperatures under High Hydrogen Pressure), *Monatsh. f. Chemie*, v. 38, 1917, pp. 359–384.

382. McADAM, D. J., JR.: Annealing Temperatures and Grain Growth, *Proc. Am. Soc. Test. Mat.*, v. 17, part 2, 1917, pp. 58–74.

383. MYLIUS, F.: Über die Herstellung reiner Metalle (The Preparation of Pure Metals), *Naturwissenschaften*, v. 5, 1917, pp. 409–417.

384. TERRY, E. M.: The Magnetic Properties of Iron, Nickel, and Cobalt above the Curie Point and Keeson's Quantum Theory of Magnetization, *Phys. Rev.*, v. 9, 1917, pp. 394–413.

385. VOGEL, R.: Über Cer-Eisenlegierungen (Gerium-iron Alloys), *Z. anorg. allgem. Chem.*, v. 99, 1917, pp. 25–49.

385A. YENSEN, T. D.: Preparation of Pure Alloys for Magnetic Purposes, *Trans. Am. Electrochem. Soc.*, v. 32, 1917, pp. 165–182.

386. YENSEN, T. D., and W. A. GATWARD: Magnetic and Other Properties of Iron-aluminum Alloys Melted in Vacuo, Univ. Illinois Exp. Sta., *Bull.* 95, 1917, 50 pp.

1918

387. GUMLICH, E.: Über die Abhängigkeit der magnetischen Eigenschaften, des spezifischen Widerstandes und der Dichte der Eisenlegierungen von der chemischen Zusammensetzung und der thermischen Behandlung (The Dependence of Magnetic Properties, Specific Resistance, and Density of Iron Alloys on Their Chemical Composition and Thermal Treatment), *Wissensch. Abhand. Phys.-Tech.*,

Reichsanstalt, v. 4, No. 3, 1918, pp. 267–420. Extract: *Stahl u. Eisen*, v. 39, 1919, pp. 765–771; 800–805; 841–847; 901–907; 966–972.

388. HOWE, H. M.: The Supposed Reversal of Inheritance of Ferrite Grain Size from That of Austenite, *Trans. Am. Inst. Min. Eng.*, v. 58, 1918, pp. 487–489.

389. IITAKA, I.: A Study of the Cementite Transformation and of the Equilibrium Diagram of the System Iron-carbon by Means of Electrical Resistance Measurement, *Sci. Rep.*, Sendai, ser. 1, v. 7, 1918, pp. 167–175.

390. JEFFRIES, Z.: Grain Size Inheritance in Iron and Carbon Steel, *Trans. Am. Inst. Min. Eng.*, v. 58, 1918, pp. 669–685.

391. KOHLSCHÜTTER, V., and E. VUILLEUMIER: Über Kathodenvorgänge bei der Metallabscheidung (Cathodic Phenomena in Metal Deposition), *Z. f. Elektrochemie*, v. 24, 1918, pp. 300–321.

392. MCADAM, D. J., JR.: Grain Size of Iron as Affected by Temperature, *Proc. Am. Soc. Test. Mat.*, v. 18, part 2, 1918, pp. 68–81.

393. SANFOURCHE, A.: Le point de Curie dans le fer pur et les ferro-siliciums (The Curie Point in Pure Iron and Silicon-iron), *C. R. Acad. Sci.*, Paris, v. 167, 1918, pp. 683–685.

394. STEAD, J. E.: Iron, Carbon and Phosphorus, *J. Iron Steel Inst.*, v. 97, 1918, pp. 389–412; discussion by J. L. Haughton, and D. Hanson, pp. 413–444.

395. WÜST, F., A. MEUTHEN, and R. DURRER: Die Temperatur-Wärmeinhaltskurven der technisch wichtigen Metalle (The Temperature versus Heat Content Curves of Technically Important Metals), *Forschungsarbeiten a. d. Gebiete d. Ingenieurwesens*, No. 204, 1918, 60 pp.

1919

396. ENGELHARDT, V.: Die deutsche Elektrotechnik in den Kriegsjahren (German Electrotechnics during the War), *Elektrotechnische Z.*, v. 40, 1919, pp. 209–211.

397. ESCARD, J.: Fabrication, propriétés et utilisation industrielle du fer électrolytique (Production, Properties, and Industrial Uses of Electrolytic Iron), *Génie Civil*, v. 75, 1919, pp. 165–171; 199–201; 225–226.

398. FETTWEIS: Über die Blaubrüchigkeit und das Altern des Eisens (Blue Brittleness and Aging of Iron), *Stahl u. Eisen*, v. 39, 1919, pp. 1–7; 34–41.

399. HAGENBACH, A., and K. LANGBEIN: Détermination de la température aux électrodes de l'arc (Determination of the Temperature of the Electrodes of the Arc), *Arch. Sci. Phys. et Naturelles*, v. 1, 1919, pp. 48–54.

400. HOLBORN, L.: Über die Abhängigkeit des Widerstandes reiner Metalle von der Temperatur (The Temperature Coefficient of Resistance of Pure Metals), *Ann. d. Physik*, ser. 4, v. 59, 1919, pp. 145–169.

401. HONDA, K.: On the Non-allotropic Nature of the A_2 Transformation in Iron, *J. Iron Steel Inst.*, v. 99, 1919, pp. 457–464.

402. HONDA, K.: On Some Physical Constants of Iron-cobalt Alloys, *Sci. Rep.*, Sendai, ser. 1, v. 8, 1919, pp. 51–58.

403. HULL, A. W.: The Crystal Structure of Ferro-magnetic Metals, *Phys. Rev.*, v. 14, 1919, pp. 540–541.

404. ISHIMOTO, M.: Investigation of Metals with Regard to Their Internal Friction, *Proc. Phys.-Math. Soc.*, Japan, ser. 3, v. 1, 1919, pp. 267–276.

405. JEFFRIES, Z.: Effect of Temperature, Deformation, and Grain Size on the Mechanical Properties of Metals, *Trans. Am. Inst. Min. Met. Eng.*, v. 60, 1919, pp. 474–562.

406. MACFADYEN, W. A.: An Aspect of Electrolytic Iron Deposition, *Trans. Faraday Soc.*, v. 15, (3), 1919–1920, pp. 98–126.

407. MONYPENNY, J. H. G.: Discussion, *J. Iron Steel Inst.*, v. 100, 1919, p. 398.

408. OBERHOFFER, P., and W. OERTEL: Die Rekristallisation des Eisens (Recrystallization of Iron), *Stahl u. Eisen*, v. 39, 1919, pp. 1061–1067.

409. RAWDON, H. S., and H. SCOTT: Microstructure of Iron and Mild Steel at High Temperatures, *National Bur. Stds. Sci. Papers*, v. 15, 1919–1920, pp. 519–528.

409A. SANFOURCHE, A.: Contribution à l'étude des ferrosiliciums (The Alloys of Iron and Silicon), *Rev. de Mét., Mém.*, v. 16, 1919, pp. 217–224.

410. VIE, G.: Propriétés et fabrication du fer électrolytique (Properties and Preparation of Electrolytic Iron), *Ann. Chim. Anal. Chim. Appl.*, ser. 2, v. 1, 1919, pp. 175–177.

1920

411. COURNOT, J.: Sur le recuit du fer électrolytique (Annealing of Electrolytic Iron), *C. R. Acad. Sci.*, Paris, v. 171, 1920, pp. 170–171. Also: *Rev. de Mét., Mém.*, v. 17, 1920, pp. 568–570.

412. FULLER, T. S.: The Penetration of Iron by Hydrogen, *General Electric Rev.*, v. 23, 1920, pp. 702–711.

413. GOERENS, P., and FR. P. FISCHER: Über Weicheisen (Soft Iron), *Elektrochemische Z.*, v. 27, 1920–1921, pp. 1–5; 11–16.

414. HOFFMANN, F., and A. SCHULZE: Über die Brauchbarkeit von Thermoelementen aus unedlen Leitern in hohen Temperaturen (Usefulness of Base Metal Thermocouples for High Temperatures), *Elektrotechnische Z.*, v. 41, 1920, pp. 427–433.

415. HUGHES, W. E.: The Electro-deposition of Metals, *Beama*, v. 6, 1920, pp. 415–420; v. 7, 1920, pp. 101–107; v. 8, 1921, pp. 133–139; 239–247; 425–431.

416. ISHIWARA, T.: On the Magnetic Determinations of A_0, A_1, A_2, and A_3 Points in Steels Containing up to 4.8 per cent of Carbon, *Sci. Rep.*, Sendai, ser. 1, v. 9, 1920, pp. 401–415.

417. NORBURY, A. L.: The Effect of Various Elements on the Electrical Resistance of Iron, *J. Iron Steel Inst.*, v. 101, 1920, pp. 627–644.

418. RAWDON, H. S., E. C. GROESBECK, and L. JORDAN: Electric-arc Welding of Steel: I. Properties of the Arc-fused Metal, *National Bur. Stds. Tech. Papers* No. 179, 1920, 63 pp.

419. RAWDON, H. S., and E. JIMENO-GIL: A Study of the Relation between the Brinell Hardness and the Grain Size of Annealed Carbon Steels, *National Bur. Stds. Sci. Papers*, v. 16, 1920, pp. 557–593.

420. Report of Subcommittee III on Inspection of the Fort Sheridan, Pittsburgh and Annapolis Tests, *Proc. Am. Soc. Test. Mat.*, v. 20, part 1, 1920, pp. 148–230.

421. RICHARDSON, W. D.: Experiments on the Corrosion of Iron and Steel, *Trans. Am. Inst. Chem. Eng.*, v. 13, (1), 1920, pp. 169–263.

422. RICHARDSON, W. D.: Rates of Solution of Iron and Steel in Non-oxidizing and Oxidizing Acids, *Trans. Am. Inst. Chem. Eng.*, v. 13, (1), 1920, pp. 265–276.

423. THOMAS, B. H.: The Electro-deposition of Iron as Applied to Motor Vehicle Repair Work, *Automobile Eng.*, v. 10, 1920, pp. 296–301. Also: *Automotive Ind.*, v. 43, 1920, pp. 418–420.

1921

424. ANDREWS, M. R.: X-ray Analysis of Three Series of Alloys, *Phys. Rev.*, v. 18, 1921, pp. 245–254.

425. AUPPERLE, J. A., and D. M. STRICKLAND: Observations on the Corrosion of Iron and Steel, *Trans. Am. Electrochem. Soc.*, v. 39, 1921, pp. 123–133.

426. BARCLAY, W. R.: Some War Experiences in the Electro-deposition of Metals, *Metal Industry* (London), v. 18, 1921, pp. 43–47; 69–70.

427. BAUER, O.: Beitrag zur Kenntnis des "Alterns" kaltgereckten Eisens (The Aging of Cold-worked Iron), *Mitt. a. d. Materialprüfungsamt*, v. 39, 1921, pp. 251–254.

428. BAUER, O.: Rostversuche mit kupferhaltigen Eisen-Blechen (Experiments on Rusting of Copper-bearing Iron Sheets), *Stahl u. Eisen*, v. 41, 1921, pp. 37–45; 76–83.

429. BAUER, O., and W. SCHNEIDER: Beitrag zur Kenntnis des Elektrolyteisens (Electrolytic Iron), *Stahl u. Eisen*, v. 41, 1921, pp. 647–648.

430. BECK, W. J.: Commercially Pure Iron in the Basic Open-hearth, *Chem. Met. Eng.*, v. 24, 1921, pp. 965–968. Also: *Iron Age*, v. 107, 1921, pp. 1462–1464.

431. BRIDGMAN, P. W.: The Effect of Pressure on the Thermal Conductivity of Metals, *Proc. Am. Acad. Arts and Sci.*, v. 57, 1921–1922, pp. 77–127.

432. BUCK, D. M.: Some Observations on the Mechanism of the Increased Corrosion Resistance of Steel and Iron Due to Small Copper Contents, *Trans. Am. Electrochem. Soc.*, v. 39, 1921, pp. 109–116.

433. CUSHMAN, A. S., and G. W. COGGESHALL: Anomalies Encountered in a Study of Immersion Tests of Iron and Steel, *Trans. Am. Electrochem. Soc.*, v. 39, 1921, pp. 81–99.

434. GUMLICH, E.: Die magnetischen Eigenschaften von Elektrolyteisen (The Magnetic Properties of Electrolytic Iron), *Stahl u. Eisen*, v. 41, 1921, pp. 1249–1254.

435. HEWLETT, C. W.: The Mass Absorption and Mass Scattering Coefficients for Homogeneous X-rays of Wave Length between 0.13 and 1.05 Ångström Units in Water, Lithium, Carbon, Nitrogen, Oxygen, Aluminum and Iron, *Phys. Rev.*, v. 17, 1921, pp. 284–301.

436. HUGHES, W. E.: Progress in the Commercial Applications of Electrolysis, *Electrician*, v. 87, 1921, pp. 640–642.

437. HUGHES, W. E.: Researches on the Electrodeposition of Iron, *Trans. Am. Electrochem. Soc.*, v. 40, 1921, pp. 185–223.

438. HUGHES, W. E.: "Slip-lines" and Twinning in Electrodeposited Iron, *J. Iron Steel Inst.*, v. 103, 1921, pp. 355–363.

439. HUGHES, W. E.: The Forms of Electrodeposited Iron and the Effect of Acid upon Its Structure, *Trans. Faraday Soc.*, v. 17, 1921–1922, pp. 442–451.

440. KÖRBER, F., and A. DREYER: Über Blaubrüchigkeit und Altern des Eisens (Blue Brittleness and Aging of Iron), *Mitt. K.-W. Inst. Eisenforschung*, v. 2, 1921, pp. 59–89.

441. MAURER, E., and W. SCHMIDT: Der Einfluss verschiedener Legierungsmetalle nebst Kohlenstoff auf einige physikalische Eigenschaften des Eisens (The Influence of Several Alloying Metals and of Carbon on Some Physical Properties of Iron), *Mitt. K.-W. Inst. Eisenforschung*, v. 2, 1921, pp. 5–20.

442. McADAM, D. J., JR.: Endurance of Steel under Repeated Stresses, *Chem. Met. Eng.*, v. 25, 1921, pp. 1081–1087.

443. MOORE, H. F., and J. B. KOMMERS: An Investigation of the Fatigue of Metals, *Univ. of Illinois Bull.*, v. 19, No. 8, October 24, 1921 (*Bull.* 124 of the Exp. Sta.), 178 pp.

444. NOYES, W. A., JR.: Some Aspects of Electrolytic Iron, *Trans. Am. Electrochem. Soc.*, v. 39, 1921, pp. 451–457.

445. PERIN, C. P., and D. BELCHER: Commercial Production of Electrolytic Iron, *Mining and Metallurgy*, No. 180, 1921, pp. 17–18.

446. RICHARDSON, E. A., and L. T. RICHARDSON: The Corrosion of Old Iron, *Trans. Am. Electrochem. Soc.*, v. 39, 1921, pp. 167–170.

447. RICHARDSON, W. D.: The Gap between Theory and Practice in the Production of Corrosion-resisting Iron and Steel, *Trans. Am. Electrochem. Soc.*, v. 39, 1921, pp. 61–79.

448. SMITH, A. W.: The Hall Effect and the Nernst Effect in Magnetic Alloys, *Phys. Rev.*, v. 17, 1921, pp. 23–37.

449. SMITS, A., and J. SPUYMAN: The Thermo-electric Determination of Transition Points, *Proc. K. Akad. Weten.*, Amsterdam, v. 23 (I), 1921, pp. 687–690.

450. SPELLER, F. N.: Practical Means of Preventing Corrosion of Iron and Steel Where not Exposed Directly to the Atmosphere, *Trans. Am. Electrochem. Soc.*, v. 39, 1921, pp. 141–150.

451. STOREY, O. W.: The Corrosion of Steel Ranges, *Trans. Am. Electrochem. Soc.*, v. 39, 1921, pp. 175–183.

452. STRAUSS, B., and A. FRY: Rissbildung in Kesselblechen (Formation of Cracks in Boiler Plate), *Kruppsche Monatshefte*, v. 2, 1921, pp. 126–136.

453. Symposium on Corrosion: *Trans. Am. Electrochem. Soc.*, v. 39, 1921, pp. 53–264.

454. WALKER, W. H.: Introduction to Symposium on Corrosion of Iron and Steel, *Trans. Am. Electrochem. Soc.*, v. 39, 1921, pp. 53–55.

455. WATTS, O. P., and H. C. KNAPP: The Effect of Copper and Silver Salts on the Corrosion of Iron by Acids, *Trans. Am. Electrochem. Soc.*, v. 39, 1921, pp. 155–160.

456. WESTGREN, A.: Roentgen Spectrographic Investigations of Iron and Steel, *J. Iron Steel Inst.*, v. 103, 1921, pp. 303–325.

457. WEVER, F.: Die Atomanordnung des Eisens in austenitischen Stahlen (The Atomic Arrangement of Iron in Austenitic Steels), *Mitt. K.-W. Inst. Eisenforschung*, v. 3, 1921, pp. 45–46.

458. WHITELEY, J. H.: Cupric Etching Effects Produced by Phosphorus and Oxygen in Iron, *J. Iron Steel Inst.*, v. 103, 1921, pp. 277–289.

459. WICKENDEN, L.: Smelting Ore by Direct Process, *Iron Tr. Rev.*, v. 69, 1921, pp. 363–368.

460. WORTH, B. G.: Unusual Boiler Tube Corrosion by Carbon Dioxide, *Trans. Am. Electrochem. Soc.*, v. 39, 1921, pp. 191–197.

1922

461. ALTERTHUM, H.: Zur Theorie der Rekristallisation (Theory of Recrystallization), *Z. f. Metallkunde*, v. 14, 1922, pp. 417–424.

462. BAIRSTOW, L.: The Fatigue of Metals, *Beama*, v. 11, 1922, pp. 652–657; 731–737; 811–818.

463. BRIDGMAN, P. W.: The Compressibility of Thirty Metals as a Function of Pressure and Temperature, *Proc. Am. Acad. Arts and Sci.*, v. 58, 1922–1923, pp. 165–242.

464. CHENEY, W. L.: Magnetic Properties of Iron-carbon Alloys as Affected by Heat Treatment and Carbon Content, *National Bur. Stds. Sci. Papers*, v. 18, 1922–1923, pp. 609–635.

465. ESTELLE, A.: The Estelle Process, *Can. Mining J.*, v. 43, 1922, pp. 672–675.

466. EUSTIS, F. A.: Electrolytic Iron from Sulphide Ores, *Chem. Met. Eng.*, v. 27, 1922, pp. 684–685.

467. FRIEND, J. N.: The Corrosion of Iron, *Iron Steel Inst., Carn. Schol. Mem.*, v. 11, 1922, 156 pp.

468. GUILLET, L., and J. COURNOT: Sur la variation des propriétés méchaniques de quelques métaux et alliages aux basses températures (The Variation of Mechanical Properties of Some Metals and Alloys at Low Temperatures), *Rev. de Mét., Mém.*, v. 19, 1922, pp. 215–221.

469. HADFIELD, SIR ROBERT: The Corrosion of Iron and Steel, *Proc. Royal Soc.* (London), ser. A, v. 101, 1922, pp. 472–486.

470. HATFIELD, W. H.: Corrosion as Affecting the Metals Used in the Mechanical Arts, *Engineer*, v. 134, 1922, pp. 639–643.

471. HUGHES, W. E.: Electrodeposition of Iron, Dept. Sci. Ind. Research, London, *Bull*. No. 6, 1922, 50 pp.

472. HUGHES, W. E.: Experiments on the Ferrous Chloride–Calcium Chloride Solution for the Electro-deposition of Iron, *Brass World*, v. 18, 1922, pp. 261–265.

473. HUGHES, W. E.: Building Up Worn Metal Parts by Electrodeposition, *Chem. Met. Eng.*, v. 26, 1922, pp. 267–269.

474. HUGHES, W. E.: Idiomorphic and Hyp-idiomorphic Structures in Electrodeposited Metal, *Trans. Am. Electrochem. Soc.*, v. 41, 1922, pp. 317–329.

475. JEFFRIES, Z.: Physical Changes in Iron and Steel below the Thermal Critical Range, *Trans. Am. Inst. Min. Met. Eng.*, v. 67, 1922, pp. 56–72.

476. KELLOGG, D. R.: Electrolytic Deposition of Iron for Building Up Worn or Undersized Parts, *Mining and Metallurgy*, v. 3, 1922, p. 61. Also: *Electric J.*, v. 19, 1922, pp. 249–251.

477. KOREF, F.: Versuche über das Weiterwachsen von Metallkristallen durch Abscheidung aus der Gasphase (Method of Growing Metal Crystals by Deposition from the Gas Phase), *Z. f. Elektrochemie*, v. 28, 1922, pp. 511–517.

478. LEA, F. C.: The Effect of Temperature on Some of the Properties of Metals, *Proc. Inst. Mech. Eng.*, 1922, pp. 885–907. Also: *Engineering*, v. 113, 1922, pp. 829–832.

479. MCMAHON, G. F.: The Manufacture of Electrolytic Iron, *Chem. Met. Eng.*, v. 26, 1922, pp. 639–641.

480. MOND, R. L., and A. E. WALLIS: Researches on the Metallic Carbonyls, *J. Chem. Soc.*, v. 121, 1922, pp. 29–32.

481. NEVILLE, R. P., and J. R. CAIN: Effects of Carbon and Manganese on the Mechanical Properties of Pure Iron, *National Bur. Stds. Sci. Papers*, v. 18, 1922–1923, pp. 411–443. Also: *Trans. Am. Electrochem. Soc.*, v. 42, 1922, pp. 21–36.

482. OBERHOFFER, P., and H. JUNGBLUTH: Die Rekristallisation des technischen Eisens (Recrystallization of Technical Iron), *Stahl u. Eisen*, v. 42, 1922, pp. 1513–1519.

483. OWEN, E. A., and G. D. PRESTON: Modification of the Powder Method of Determining the Structure of Metal Crystals, *Proc. Phys. Soc.* (London), v. 35, 1922–1923, pp. 101–108.

484. PFANHAUSER, W.: "Die elktrolytischen Metallniederschläge. Lehrbuch der Galvanotechnik mit Berücksichtigung der Behandlung der Metalle vor und nach dem Elektroplattieren," Julius Springer, Berlin, 6th ed., 1922, 828 pp.

485. PILLING, N. B.: Effect of Heat Treatment on the Hardness and Microstructure of Electrolytically Deposited Iron, *Trans. Am. Electrochem. Soc.*, v. 42, 1922, pp. 9–17.

486. POLANYI, M.: Verfestigung von Einzelkristallen durch mechanische Bearbeitung (Strain Hardening of Single Crystals), *Z. f. Elektrochemie*, v. 28, 1922, pp. 16–20.

487. RAWDON, H. S., and A. I. KRYNITSKY: Resistance to Corrosion of Various Types of Chromium Steels, *Chem. Met. Eng.*, v. 27, 1922, pp. 171–173.

488. SAUERWALD, F.: Die ohne vorhergehende Kaltbearbeitung eintretende Kornvergrösserung in metallischen Körpern die aus pulverförmigem Material durch Druck oder Sinterung erhalten werden (Grain Growth Not Preceded by Cold Work in Metallic Bodies That Have Been Prepared by Pressing or Sintering), *Z. anorg. allgem. Chem.*, v. 122, 1922, pp. 277–294.

489. SCOTT, H.: What is Steel? *Chem. Met. Eng.*, v. 27, 1922, p. 1156.

490. SOUDER, W., and P. HIDNERT: Thermal Expansion of a Few Steels, *National Bur. Stds. Sci. Papers*, v. 17, 1922, pp. 611–626.

491. STOUGHTON, B.: Electrolytic Iron a Commercial Product, *Iron Age*, v. 109, 1922, pp. 32–36.

492. THOMPSON, F. C., and E. WHITEHEAD: On the Changes in Iron and Steel at Temperatures below 280°C., *Proc. Royal Soc.* (London), ser. A, v. 102, 1922–1923, pp. 587–599.

493. WESTGREN, A., and G. PHRAGMÉN: X-ray Studies on the Crystal Structure of Steel, *J. Iron Steel Inst.*, v. 105, 1922, pp. 241–262.

1923

494. ALLEY, J. D.: Saving Worn Parts by Electro-deposition, *Brass World*, v. 19, 1923, pp. 373–375. Also: *Machinery*, New York, v. 30, 1923–1924, pp. 202–204.

495. ARNOLD, H. D., and G. W. ELMEN: Permalloy, an Alloy of Remarkable Magnetic Properties, *J. Franklin Inst.*, v. 195, 1923, pp. 621–632.

496. AUPPERLE, J. A.: Discussion of C. B. Sawyer's Paper on Nitrogen in Steel, *Trans. Am. Inst. Min. Met. Eng.*, v. 69, 1923, pp. 828–830.

497. BENSON, L. E., and F. C. THOMPSON: Some Experiments on Grain Growth in Iron and Steel (Part I), *J. Iron Steel Inst.*, v. 107, 1923, pp. 525–543.

498. BERLINER, J. F. T.: Preparation and Properties of Pure Iron Alloy. IV. Determination of the Critical Ranges of Pure Iron-carbon Alloys by the Thermo-electric Method, *National Bur. Stds. Sci. Papers*, v. 19, 1923–1924, pp. 347–356.

498A. BLUM, W., and H. S. RAWDON: The Crystalline Form of Electro-deposited Metals, *Trans. Am. Electrochem. Soc.*, v. 44, 1923, pp. 397–425.

499. BOUCHAYER, A.: Le fer électrolytique "Bêve" (Electrolytic Iron), *Mém. Soc. Ing. Civils de France*, v. 76, 1923, pp. 557–592.

500. BOUCHAYER, A.: Le fer électrolytique, ses applications (Electrolytic Iron, Its Uses), *Rev. de Mét.*, *Mém.*, v. 20, 1923, pp. 434–438.

501. CALCOTT, W. S., J. C. WHETZEL, and H. F. WHITTAKER: "Corrosion Tests and Materials of Construction for Chemical Engineering Apparatus," D. Van Nostrand Co., New York, 1923, 182 pp.

502. CAMPBELL, E. D., J. F. ROSS, and W. L. FINK: The Relative Efficiency of Dry and Moist Hydrogen on the Decarburization of Steel

at 950°C., and the Effect of Hydrogen on the Phosphorus Content, *J. Iron Steel Inst.*, v. 108, 1923, pp. 179–185.

503. CAMPBELL, L. L.: "Galvanomagnetic and Thermomagnetic Effects," Longmans, Green and Co., New York, 1923, p. 231, 311 pp.

504. CONDER, H.: Roasting Ores in Hydrogen, *Eng. Min. Press*, v. 116, 1923, pp. 943–944.

505. EVANS, U. R.: The Electrochemical Character of Corrosion, *J. Inst. Metals*, v. 30, 1923, pp. 239–282.

506. EVANS, U. R.: The Mechanism of the So-called "Dry Corrosion" of Metals, *Trans. Faraday Soc.*, v. 19, 1923–1924, pp. 201–212.

507. FISCHER, F. P.: Rekristallisationsversuche allgemeiner Art und zahlenmässige Feststellungen über Festigkeitseigenschaften rekristallisierten Flusseisens (Weicheisens) (Recrystallization Investigations in General and Numerical Determinations of the Mechanical Properties of Recrystallized Ingot Iron), *Kruppsche Monatshefte*, v. 4, 1923, pp. 77–114.

507A. FRAICHET, L.: Aimantation et déformations moléculaires de l'acier à la traction. Limite élastique (Magnetization and Molecular Deformation of Steel under Tensile Stress. The Elastic Limit), *Rev. de Mét., Mém.*, v. 20, 1923, pp. 32–45.

507B. FRAICHET, L.: Essai magnétique des aciers à la traction. Limites élastiques (Magnetic Testing of Steels under Tensile Stress. The Elastic Limit), *Rev. de Mét., Mém.*, v. 20, 1923, pp. 549–559.

508. FRIEND, J. N.: Second Report on the Relative Corrodibilities of Various Commercial Forms of Iron and Steel, *Iron Steel Inst., Carn. Schol. Mem.*, v. 12, 1923, pp. 1–25.

509. FRY, A.: Stickstoff in Eisen, Stahl und Sonderstahl. Ein neues Oberflächenhärtungsverfahren (Nitrogen in Iron, Steel and Special Steels. A New Surface-hardening Method), *Stahl u. Eisen*, v. 43, 1923, pp. 1271–1279. Also: *Kruppsche Monatshefte*, v. 4, 1923, pp. 137–151.

510. GOFFEY, A., and F. C. THOMPSON: The Changes in Iron and Steel below 400°C., *J. Iron Steel Inst.*, v. 107, 1923, pp. 465–488.

511. GOUGH, H. J., and D. HANSON: The Behavior of Metals Subjected to Repeated Stresses, *Proc. Royal Soc.* (London), ser. A, v. 104, 1923, pp. 538–565.

512. HANSON, D., and J. R. FREEMAN: The Constitution of the Alloys of Iron and Nickel, *J. Iron Steel Inst.*, v. 107, 1923, pp. 301–314.

513. HEAPS, C. W.: The Effect of Crystal Structure on Magnetostriction, *Phys. Rev.*, v. 22, 1923, pp. 486–501.

514. HINELINE, H. D.: Notes on the Electrodeposition of Iron, *Trans. Am. Electrochem. Soc.*, v. 43, 1923, pp. 119–125.

515. HUGHES, W. E.: The Electro-deposition of Metals, *Electrician*, v. 91, 1923, pp. 628–630.

516. HUGHES, W. E.: Corrosion of Electrolytic Iron, *Chem. Met. Eng.*, v. 29, 1923, pp. 536–537.

517. HUGHES, W. E.: "Modern Electroplating," H. Frowde and Hodder and Stoughton, London, 1923, 160 pp.

518. Knobel, M., P. Caplan, and M. Eiseman: The Effect of Current Density on Overvoltage, *Trans. Am. Electrochem. Soc.*, v. 43, 1923, pp. 55–74.

519. Kreutzberg, E. C.: Making Iron from Ore by a New Electrolytic Process, *Iron Tr. Rev.*, v. 73, 1923, pp. 595–598.

520. Langenberg, F. C.: An Investigation of the Behavior of Certain Steels under Impact at Different Temperatures, *Iron Steel Inst., Carn. Schol. Mem.*, v. 12, 1923, pp. 75–108.

521. Masing, G.: Rekristallisation von Metallen (Recrystallization of Metals), *Naturwissenschaften*, v. 11, 1923, pp. 413–422.

522. McAdam, D. J., Jr.: Endurance Properties of Steel, *Proc. Am. Soc. Test. Mat.*, v. 23, part 2, 1923, pp. 56–105.

523. McKeehan, L. W.: The Crystal Structure of Iron-nickel Alloys, *Phys. Rev.*, v. 21, 1923, pp. 402–407.

524. Moore, H. F., and T. M. Jasper: An Investigation of the Fatigue of Metals, *Univ. of Illinois Bull.*, v. 20, No. 37, May 14, 1923 (*Bull.* 136 of the Exp. Sta.), 97 pp.

525. Müller, R., R. Hönig, and A. Konetschnigg: Zur Elektrochemie nichtwässeriger Lösungen. V. Versuche zur elektrolytischen Abscheidung einiger Schwermetalle aus Lösungen in wasserfreiem Pyridin (Electrochemistry of Non-aqueous Solutions. V. Attempts to Deposit by Electrolysis Certain Heavy Metals from Anhydrous Pyridine), *Monatsh. f. Chemie*, v. 44, 1923, pp. 237–245.

526. Norbury, A. L.: The Hardness of Annealed Copper, *J. Inst. Metals*, v. 29, 1923, pp: 407–435.

527. Oberhoffer, P., and A. Gallaschik: Beitrag zur Kenntnis der Eisen-Arsen Legierungen (Iron-arsenic Alloys), *Stahl u. Eisen*, v. 43, 1923, pp. 398–400.

528. O'Neill, H.: Hardness Tests on Crystals of Aluminum, *J. Inst. Metals*, v. 30, 1923, pp. 299–305.

529. Pilling, N. B., and R. E. Bedworth: The Oxidation of Metals at High Temperatures, *J. Inst. Metals*, v. 29, 1923, pp. 529–582.

530. Richtmyer, F. K., and F. W. Warburton: The Absorption of X-rays by Iron, Cobalt, Nickel and Copper, *Phys. Rev.*, v. 22, 1923, pp. 539–545.

531. Sawyer, C. B.: Nitrogen in Steel, *Trans. Am. Inst. Min. Met. Eng.*, v. 69, 1923, pp. 798–828.

532. Sirovich, G.: La trasformazione polimorfica del ferro a 370°C. e la possibilita di soluzione della cementite nel ferro (A Polymorphic Transformation of Ferrite at 370°C. and the Possibility of the Solution of Cementite in Ferrite), *Gazz. Chim. Ital.*, v. 53, 1923, pp. 674–688.

533. Stribeck, R.: Dauerfestigkeit von Eisen und Stahl bei wechselnder Biegung, verglichen mit den Ergebnissen des Zugversuchs (Fatigue Strength of Iron and Steel in Alternating Bending Compared with the Results of Tensile Tests), *Z. Ver. deutsch. Ing.*, v. 67, 1923, pp. 631–636.

534. Traill, R. J.: Development of Electrolytic Iron, *Can. Chem. Met.*, v. 7, 1923, pp. 181–182.

535. Traill, R. J.: The Hydrometallurgical Treatment of Iron Sulphide Ores, *Can. Dept. Mines, Mines Br. Rep.* No. 617, 1923, pp. 101–114.

536. Vanick, J. S.: Deterioration of Steel and Wrought Iron Tubes in Hot Gaseous Ammonia, *Trans. Am. Soc. Steel Treat.*, v. 4, 1923, pp. 62–78.

537. Vernon, W. H. J.: First Report to the Atmospheric Corrosion Research Committee, *Trans. Faraday Soc.*, v. 19, 1923–1924, pp. 839–900.

538. Whitfield, R.: Direct Production of Iron and Steel, *Iron Coal Tr. Rev.*, v. 106, 1923, p. 6–7.

1924

539. Ahmad, N.: Absorption of Hard Gamma Rays by Elements, *Proc. Royal Soc.* (London), ser. A, v. 105, 1924, pp. 507–519.

540. Allen, S. J. M.: The Absorption Coefficients of Homogeneous X-rays between Wave Lengths of 0.1 Å. and 0.71 Å., *Phys. Rev.*, v. 24, 1924, pp. 1–8.

541. Andrew, J. H., and A. J. K. Honeyman: The Specific Volume of Steels, *Iron Steel Inst., Carn. Schol. Mem.*, v. 13, 1924, pp. 253–266.

542. Anon.: Studies Direct Reduction of Ore, *Iron Tr. Rev.*, v. 74, 1924, pp. 1635–1636.

543. Audubert, R.: La structure des dépôts électro-chimiques (The Structure of Electrochemical Deposits), *Rev. de Mét., Mém.*, v. 21, 1924, pp. 567–584.

544. Bain, E. C.: The Nature of Martensite, *Trans. Am. Inst. Min. Met. Eng.*, v. 70, 1924, pp. 25–35.

545. Bancroft, W. D.: The Electrolytic Theory of Corrosion, *J. Phys. Chem.*, v. 28, 1924, pp. 785–871.

546. Belcher, D.: Progress in Electrolytic Iron, *Trans. Am. Electrochem. Soc.*, v. 45, 1924, pp. 455–470.

547. Benedicks, C., D. W. Berlin, and G. Phragmén: A Method for the Determination of the Specific Gravity of Liquid Iron and Other Metals of High Melting Point, *Iron Steel Inst., Carn. Schol. Mem.*, v. 13, 1924, pp. 129–166.

548. Blum, W., and G. B. Hogaboom: "Principles of Electroplating," McGraw-Hill Book Company, Inc., New York, 1924, 356 pp.

549. Borelius, G., and F. Gunneson: Temperature Periods in the Emission of Occluded Gases from Iron, *Nature*, v. 113, 1924, pp. 82–83.

550. Danielson, N.: Swedish Charcoal Iron, *Mining and Metallurgy*, v. 5, 1924, pp. 569–572.

551. Davey, W. P.: Precision Measurements of Lattice Constants of Pure Metals, *Phys. Rev.*, v. 23, 1924, p. 292.

552. Duhme, E.: Über die elektrolytische Darstellung reinsten Eisens (The Electrolytic Preparation of Pure Iron), *Wiss. Veröff. Siemens-Konzern*, v. 3, part 2, 1924, pp. 39–42.

553. EDWARDS, C. A., and L. B. PFEIL: The Production of Large Crystals by Annealing Strained Iron, *J. Iron Steel Inst.*, v. 109, 1924, pp. 129–147.

554. EVANS, U. R.: "Corrosion of Metals," Longmans Green and Co., New York, 1924, 212 pp.

555. FORNANDER, E.: The Direct Production of Iron, *Chem. Met. Eng.*, v. 30, 1924, pp. 864–868; 907–910.

556. FRIEND, J. N., and W. E. THORNEYCROFT: Examination of Iron from Konarak, *J. Iron Steel Inst.*, v. 110, 1924, pp. 313–315.

557. FRÖLICH, P. K.: The Introduction of Carbonaceous Matter in Electrodeposited Iron and Nickel, *Trans. Am. Electrochem. Soc.*, v. 46, 1924, pp. 87–103.

558. FUKUDA, M.: Magnetic and Electric Properties of Electrolytic Iron and Its Alloys Melted in Vacuo and Rolled into Sheet, *J. Inst. Elec. Eng., Japan*, No. 435, 1924, pp. 978–1007. Abst.: *Sci. Abstracts*, v. A28, 1925, p. 145.

559. GLOCKER, R., and E. KAUPP: Über die Faserstruktur elektrolytischer Metallniederschläge (The Fibrous Structure of Metallic Electrodeposits), *Z. f. Physik*, v. 24, 1924, pp. 121–139.

560. GOERENS, P.: Die Kesselbaustoffe (Materials for Boiler Construction), *Z. Ver. deutsch. Ing.*, v. 68, 1924, pp. 41–47.

561. GOETZ, A.: Das thermoelektrische Verhalten des reinen Eisens an seinen Umwandlungspunkten (The Thermo-electric Behavior of Iron at Its Transformation Points), *Physik. Z.*, v. 25, 1924, pp. 562–571. Extract: *Landolt-Börnstein Tab.*, v. 1, 1927, p. 555.

562. GOUGH, H. J.: "The Fatigue of Metals," Scott, Greenwood & Son, London, 1924, 304 pp.

563. GROSS, R.: Verfestigung und Rekristallisation (Strengthening and Recrystallization), *Z. f. Metallkunde*, v. 16, 1924, pp. 344–352.

564. HADFIELD, SIR ROBERT: Discussion of paper by D. J. MacNaughton on The Hardness of Electro-deposited Iron, Nickel, Cobalt, and Copper, *J. Iron Steel Inst.*, v. 109, 1924, pp. 425–427.

565. HATTA, S.: A New Method of Manufacturing Thin Sheet Iron, *J. Jap. Soc. Chem. Ind.*, v. 27, 1924, p. 565 (In Japanese. Discussed by Pfanhauser[932]).

566. HEINDLHOFER, K.: Crystal Structure of Hard Steel, *Phys. Rev.*, v. 24, 1924, pp. 426–438.

567. HUTCHINS, T. W. S.: Electrolytic Iron, *Trans. First World Power Conference*, v. 4, 1924, pp. 704–731. Also: *World Power*, v. 2, 1924, pp. 341–347.

568. KÖRBER, F., and W. ROHLAND: Über den Einfluss von Legierungszusätzen und Temperaturänderungen auf die Verfestigung von Metallen (The Influence of Alloy Additions and of Temperature Changes on the Strengthening of Metals), *Mitt. K.-W. Inst. Eisenforschung*, v. 5, 1924, pp. 55–68.

569. KÖRBER, F., and I. B. SIMONSEN: Dynamische Prüfung des Stahles bei höheren Temperaturen (The Dynamic Testing of Steels at Elevated Temperatures), *Mitt. K.-W. Inst. Eisenforschung*, v. 5, 1924, pp. 21–35.

570. MacNaughton, D. J.: The Hardness of Electrodeposited Iron, Nickel and Cobalt, *J. Iron Steel Inst.*, v. 109, 1924, pp. 409–423.

571. Mailänder, R.: Der Einfluss der Probenbreite auf die Kerbzähigkeit von Flusseisen (The Effect of the Width of Specimen on the Notch Brittleness of Ingot Iron), *Kruppsche Monatshefte*, v. 5, 1924, pp. 16–21.

572. McLare, J. P.: Repair of Worn Components by Electro-deposition, *Trans. Faraday Soc.*, v. 20, 1924, pp. 87–96. Abst.: *Electrician*, v. 92, 1924, pp. 594–595.

573. Merrils, F. S.: Studies in the Fatigue of Metals, *Iron Steel Inst., Carn. Schol. Mem.*, v. 13, 1924, pp. 83–128.

574. Oberhoffer, P., and W. Oertel: Die Rekristallisation des Elektrolyteisens (Recrystallization of Electrolytic Iron), *Stahl u. Eisen*, v. 44, 1924, pp. 560–561.

575. O'Neill, H.: The Effect of Cold Work upon the Density of Crystals of Alpha Iron, *J. Iron Steel Inst.*, v. 109, 1924, pp. 93–108.

576. Pollitt, A. A.: "The Causes and Prevention of Corrosion," D. Van Nostrand Co., New York, 1924, 230 pp.

577. Richards, T. W., and W. T. Richards: The Effect of a Magnetic Field on the Potential of Hydrogen Occluded by Iron, *J. Am. Chem. Soc.*, v. 46, 1924, pp. 89–104.

578. Richardson, N., and E. K. MacNutt: Effect of Temperature on the Impact Resistance of Low Carbon Steels Deformed at Different Temperatures, *Trans. Am. Soc. Steel Treat.*, v. 5, 1924, pp. 348–361.

579. Rooney, T. E.: The Estimation of Oxygen in Pure Iron, *J. Iron Steel Inst.*, v. 110, 1924, pp. 122–128.

580. Sauerwald, F.: Die Herstellung synthetischer Metallkörper durch Druck oder Sinterung (Production of Synthetic Metallic Substances by Pressure or by Sintering), *Z. f. Metallkunde,* v. 16, 1924, pp. 41–46.

581. Sedström, E.: Dissertation, Stockholm, 1924. Cited in Abegg's "Handbuch der anorganischen Chemie," S. Hirzel, Leipzig, 1931, v. 4, sec. 3, part 2, p. A191.

582. Skowronski, S.: Improvements in Electrolytic Refining during the Last Decade, *Trans. Am. Electrochem. Soc.*, v. 45, 1924, pp. 353–364.

583. Tammann, G., and N. Nikitin: Über die Pyrophorität von Metallpulvern (Pyrophoric Properties of Metal Powders), *Z. anorg. allgem. Chem.*, v. 135, 1924, pp. 201–204.

584. Traill, R. J., and W. R. McClelland: The Hydrometallurgical Treatment of Iron Sulphide Ore for the Production of Electrolytic Iron and Recovery of Sulphur, *Can. Dept. Mines, Mines Br. Rep.* No. 643, 1924, pp. 92–102.

585. Tritton, F. S., and D. Hanson: Ferrous Alloys Research, Part II. Iron and Oxygen, *J. Iron Steel Inst.*, v. 110, 1924, pp. 90–121.

586. Westgren, A., and G. Phragmén: X-ray Studies of the Crystal Structure of Steel, *J. Iron Steel Inst.*, v. 109, 1924, pp. 159–172.

587. WEVER, F.: Zur Konstitution des technischen Eisens (The Constitution of Technical Iron), *Z. f. Elektrochemie*, v. 30, 1924, pp. 376–382.

588. WILLIAMS, R. S., and V. O. HOMERBERG: Intercrystalline Fracture of Steel, *Trans. Am. Soc. Steel Treat.*, v. 5, 1924, pp. 399–412.

589. YEH, C. S.: The Effect of Hydrostatic Pressure on the Magnetic Permeability of Iron, Cobalt and Nickel, *Proc. Am. Acad. Arts and Sci.*, v. 60, 1924–1925, pp. 503–533.

590. YENSEN, T. D.: Magnetic Properties of the Ternary Alloys Fe-Si-C, *Trans. Am. Inst. Elec. Eng.*, v. 43, 1924, pp. 145–171.

591. YOUNG, J.: The Thomson Effect in Copper, Iron and Carbon Steels, *Proc. Phys. Soc.* (London), v. 37, 1924–1925, pp. 145–157.

1925

592. ANON.: Making Pure Iron Commercially, *Iron Age*, v. 116, 1925, pp. 675–679.

593. ANON.: Machine for Slitting and Coiling Tubes, *Iron Age*, v. 116, 1925, pp. 1317–1318.

594. ATEN, A. H. W., H. J. DEN HERTOG, and L. WESTENBERG: Electro-deposition of Metals from Fused Electrolytes, *Trans. Am. Electrochem. Soc.*, v. 47, 1925, pp. 265–274.

595. BLAKE, F. C.: Precision X-ray Measurements by the Powder Method, *Phys. Rev.*, v. 26, 1925, pp. 60–70.

596. BOZORTH, R. M.: The Orientations of Crystals in Electrodeposited Metals, *Phys. Rev.*, v. 26, 1925, pp. 390–400.

597. BRACE, P. H.: A High Frequency Induction Furnace Plant for the Production of Special Alloys, *J. Am. Inst. Elec. Eng.*, v. 44, 1925, pp. 992–1001.

598. CAIN, J. R., and A. A. PETERSON: A Laboratory High Frequency Furnace, *Trans. Am. Electrochem. Soc.*, v. 48, 1925, pp. 139–152.

599. CAMPBELL, E. D.: A Study of the Correlation of the Remanent Magnetism and Specific Resistance of Some Pure Iron-carbon Alloys, *Trans. Faraday Soc.*, v. 21, 1925, pp. 338–348.

600. CAZAUD, R., and R. HUGUES: Contribution à l'étude du fer électrolytique: Influence du recuit sur les propriétés méchaniques et magnétiques: Étude micrographique (Contribution to the Study of Electrolytic Iron: The Influence of Annealing on the Mechanical and Magnetic Properties: Micrographic Study), *Rev. de Mét., Mém.*, v. 22, 1925, pp. 218–222.

601. COURNOT, J., and K. SASAGAWA: Contribution à l'étude de la viscosité des alliages à température élevée (The Viscosity of Alloys at Elevated Temperatures), *Rev. de Mét., Mém.*, v. 22, 1925, pp. 753–763.

602. DAVEY, W. P.: Precision Measurements of the Lattice Constants of Twelve Common Metals, *Phys. Rev.*, v. 25, 1925, pp. 753–761.

603. EDWARDS, C. A., and L. B. PFEIL: The Tensile Properties of Single Iron Crystals and the Influence of Crystal Size upon the Tensile Properties of Iron, *J. Iron Steel Inst.*, v. 112, 1925, pp. 79–110.

604. ESSER, H., and P. OBERHOFFER: Zur Kenntnis der binären Systeme Eisen-Silizium, Eisen-Phosphor und Eisen-Mangan (The Binary

Systems, Iron-silicon, Iron-phosphorus, and Iron-manganese), *Ber. Fachausschüsse des Vereins deutscher Eisenhüttenleute, Werkstoffausschuss,* Rep. 69, 1925, 7 pp.

605. FISCHVOIGT, H., and F. KOREF: Versuche über das Weiterwachsen von Metallkristallen durch Abscheidung aus der Gasphase. II. (Method of Growing Metal Crystals by Deposition from the Gas Phase), *Z. tech. Physik,* v. 6, 1925, pp. 296–298.

606. FLODIN, H.: A New Direct Process for the Manufacture of Steel, *J. Iron Steel Inst.,* v. 112, 1925, pp. 9–25.

607. FREEMAN, J. R., and R. D. FRANCE: Comparative Cold-rolling Tests of Open-hearth Steel Strip (Deep Drawing Stock) and Electrolytic Iron Strip, *National Bur. Stds. Tech. Papers,* v. 19, 1925, pp. 297–313.

608. FRIEND, J. N., and W. E. THORNEYCROFT: Ancient Iron from Richborough and Folkestone, *J. Iron Steel Inst.,* v. 112, 1925, pp. 225–232.

609. FRÖLICH, P. K.: Carbon Error in the Quantitative Deposition of Nickel and Iron from Complex Oxalate Electrolytes, *Analyst,* v. 50, 1925, pp. 224–230.

610. FUJIHARA, T.: Rôle of Carbon Dioxide in Corrosion of Iron, *Chem. Met. Eng.,* v. 32, 1925, pp. 810–811.

611. GALIBOURG, J.: Thermo-électricité des métaux et alliages (Thermoelectricity of Metals and Alloys), *Rev. de Mét., Mém.,* v. 22, 1925, pp. 400–434.

612. GERLACH, W.: Die magnetischen Eigenschaften von Eiseneinkristallen (Magnetic Properties of Single Iron Crystals), *Physik. Z.,* v. 26, 1925, pp. 914–915.

613. GREAVES, R. H., and J. A. JONES: The Effect of Temperature on the Behavior of Iron and Steel in the Notched Bar Impact Test, *J. Iron Steel Inst.,* v. 112, 1925, pp. 123–162.

614. JENKIN, C. F.: High Frequency Fatigue Tests, *Proc. Royal Soc.* (London), ser. A, v. 109, 1925, pp. 119–143.

615. KÖRBER, F., and A. POMP: Einfluss der Vorbehandlung auf die Kerbzähigkeit des Flusseisens in der Kälte und Wärme (The Influence of Previous Treatment on the Notch Brittleness of Ingot Iron at Low and High Temperatures), *Mitt. K.-W. Inst. Eisenforschung,* v. 6, 1925, pp. 33–43.

616. KREUTZBERG, E. C.: Introduces Electrolytic Iron to Wider Usefulness, *Iron Tr. Rev.,* v. 77, 1925, pp. 1207–1210; 1214.

617. KRIVOBOK, V. N.: Thermal Disturbances and Recrystallization of Cold-worked Steels, *Trans. Am. Soc. Steel Treat.,* v. 8, 1925, pp. 703–720.

618. KUTSCHER, G.: Glühhitzeschutz von Eisenteilen durch das Metallspritzverfahren (Protection of Iron Parts at a Red Heat by Metal Spraying Process), *Keram. Rundschau,* v. 33, 1925, pp. 55–56. Abst.: *J. Inst. Metals,* v. 36, 1926, p. 473.

619. LANGMUIR, I.: Flames of Atomic Hydrogen, *Science,* v. 62, 1925, pp. 463–464.

620. LUDWIK, P., and R. SCHEU: Über die Streckgrenze von Elektrolyt-
und Flusseisen (The Yield Strength of Electrolytic Iron and Ingot
Iron), *Ber. Fachausschüsse des Vereins deutscher Eisenhüttenleute,
Werkstoffausschuss*, Rep. 70, 1925, 7 pp.

621. MABEE, H. C., and A. E. SMALL: A Combined Pyro- and Hydro-
metallurgy Process for the Treatment of Nickel, Ferrous Pyrrhotite
Ores, and Other Ores, *Can. Dept. Mines, Mines Br. Rep.* 670, 1925,
pp. 89–94.

622. MARTIN, L. H.: Some Measurements on the Absorption of X-rays
of Long Wave Length, *Proc. Cambridge Phil. Soc.*, v. 23, 1925,
pp. 783–793.

623. MASING, G.: Rekristallisation und Erholung (Kristallvergütung)
bei Metallen (Recrystallization and Recovery of Crystalline
Properties in Metals), *Wiss. Veröff. Siemens-Konzern*, v. 4, (II),
1925, pp. 230–243.

623*A*. MCCORKLE, P.: Anhysteretic Magnetostrictive Effects in Iron,
Nickel, and Cobalt, *Phys. Rev.*, v. 25, 1925, pp. 541–549.

624. MEHL, R. F., J. L. WHITTEN, and D. P. SMITH: Laboratory Produc-
tion of Pure Magnesia Ware, *J. Ind. Eng. Chem.*, v. 17, 1925,
pp. 1171–1172.

625. MILLAR, R. A.: Vapor Pressures of Some Liquid and Solid Metals,
J. Ind. Eng. Chem., v. 17, 1925, pp. 34–35.

626. RANE, M. B., and M. PRASAD: The Effect of the Addition of Some
Alkaloids on the Rate of Solution of Iron in Dilute Hydrochloric
Acid, *J. Phys. Chem.*, v. 29, 1925, pp. 249–255.

627. REED, E. L.: An Investigation of Properties of Iron-carbon Alloys,
Iron Steel Inst., Carn. Schol. Mem., v. 14, 1925, pp. 91–130.

628. RODEBUSH, W. H., and J. C. MICHALEK: The Atomic Heat Capacities
of Iron and Nickel at Low Temperatures, *J. Am. Chem. Soc.*, v. 47,
1925, pp. 2117–2121.

629. RUER, R., and K. BODE: Die magnetischen Umwandlungen der ferro-
magnetischen Metalle (The Magnetic Transformations of Ferro-
magnetic Metals), *Stahl u. Eisen*, v. 45, 1925, pp. 1184–1188.

630. SATÔ, S.: Dilatometric Investigation of the A_3 and A_4 Transforma-
tions in Pure Iron, *Sci. Rep.*, Sendai, ser. 1, v. 14, 1925, pp. 513–
527. Also: *Phil. Mag.*, v. 1, 1926, pp. 996–1007.

631. SAUERWALD, F., and G. NEUENDORFF: Über die Gewinnung der
Schwermetalle durch Schmelzflusselektrolyse. I. Die Gewinnung
von Eisen (Production of Heavy Metals from Fused Electrolytes.
I. The Production of Iron), *Z. f. Elektrochemie*, v. 31, 1925, pp. 643–
646.

632. SAUVEUR, A., and D. C. LEE: Influence of Strain and of Heat on the
Hardness of Iron and Steel, *J. Iron Steel Inst.*, v. 112, 1925, pp.
323–329.

633. SHIPLEY, J. W., I. R. MCHAFFIE, and N. D. CLARE: Corrosion of
Iron in the Absence of Oxygen, *J. Ind. Eng. Chem.*, v. 17, 1925,
pp. 381–385.

634. SMITS, A., and A. WALLAGH: The Pyrophoric Phenomena in Iron, *Rec. Trav. Chim. des Pays-Bas*, v. 44, 1925, pp. 130–131.

635. TRAILL, R. J., and W. R. McCLELLAND: Hydrometallurgical Treatment of Iron Sulphide Ores for the Production of Electrolytic Iron, *Can. Dept. Mines, Mines Br. Rep.* 670, 1925, pp. 72–77.

636. TRAILL, R. J., W. R. McCLELLAND, and E. A. THOMPSON: New Process for the Treatment of Ilmenite for the Recovery of Electrolytic Iron and Titanium Oxide, *Can. Dept. Mines, Mines Br. Rep.* 670, 1925, pp. 81–88.

637. TRITTON, F. S.: A Centrifugal Method of Making Small Pots of Electrically Fused Refractory Materials, *Proc. Royal Soc.* (London), ser. A, v. 107, 1925, pp. 287–290.

638. UTIDA, T., and M. SAITO: The Influence of Metallic Elements on the Corrosion of Iron and Steel, *Sci. Rep.*, Sendai, ser. 1, v. 14, 1925, pp. 295–312.

639. WEBSTER, W. L.: Magnetic Properties of Iron Crystals, *Proc. Royal Soc.* (London), ser. A, v. 107, 1925, pp. 496–509.

640. WEBSTER, W. L.: Magnetostriction in Iron Crystals, *Proc. Royal Soc.* (London), ser. A, v. 109, 1925, pp. 570–584.

641. WEVER, F., and W. REINECKEN: Beiträge zur Kenntnis des Systems Eisen-Zinn (The Iron-tin System), *Mitt. K.-W. Inst. Eisenforschung*, v. 7, 1925, pp. 69–79.

642. WHITMAN, W. G.: Corrosion of Iron, *Chem. Review*, v. 2, 1925–1926, pp. 419–435.

643. WHITMAN, W. G., and R. P. RUSSELL: The Acid Corrosion of Metals, *J. Ind. Eng. Chem.*, v. 17, 1925, pp. 348–354.

644. WHITMAN, W. G., R. P. RUSSELL, and G. H. B. DAVIS: The Solubility of Ferrous Hydroxide and Its Effect upon Corrosion, *J. Am. Chem. Soc.*, v. 47, 1925, pp. 70–79.

645. WYCKOFF, R. W. G., and E. D. CRITTENDEN: An X-ray Examination of Some Ammonia Catalysts, *J. Am. Chem. Soc.*, v. 47, 1925, pp. 2866–2882.

1926

646. ALLEN, S. J. M.: The Absorption of X-rays of Wave Length down to 0.08 Å., *Phys. Rev.*, v. 27, 1926, pp. 266–276.

647. ALLEN, S. J. M.: Absorption of X-rays from $\lambda = .08$ to 4.0 Å., *Phys. Rev.*, v. 28, 1926, pp. 907–922.

648. ANON.: Steel Direct from Ore, *Iron Age*, v. 118, 1926, p. 1227.

649. BAIN, E. C.: The Nature of the Alloys of Iron and Chromium, *Trans. Am. Soc. Steel Treat.*, v. 9, 1926, pp. 9–32.

650. BENEDICKS, C.: "Metallographic Researches," McGraw-Hill Book Company, Inc., New York, 1926, pp. 205–217.

651. BENEDICKS, C., H. BÄCKSTRÖM, and P. SEDERHOLM: Anomalies in Heat Conduction as Investigated in Spherical Steel Specimens with Some Determinations of Thermal (and Electrical) Conductivity in Iron and Carbon Steels, *J. Iron Steel Inst.*, v. 114, 1926, pp. 127–172.

652. BERLIN, D. W.: Some Determinations of the Specific Gravity of Iron and Low-carbon Steel in a Molten Condition, *Iron Steel Inst., Carn. Schol. Mem.*, v. 15, 1926, pp. 1–16.

653. CAMPBELL, E. D., and H. W. MOHR: The Specific Resistance and the Thermoelectromotive Potential of Some Steels Differing Only in Carbon Content, *J. Iron Steel Inst.*, v. 113, 1926, pp. 375–392.

654. CARPENTER, H. C. H.: Methods of Growing Large Metal Crystals, *J. Inst. Metals*, v. 35, 1926, pp. 409–438. Also: *Metal Industry* (London), v. 29, 1926, pp. 409–411; 437–439.

655. COMPTON, A. H.: "X-rays and Electrons," D. Van Nostrand Co., New York, 1926, pp. 180 and 185.

656. DAVEY, W. P.: A Study of Crystal Structure and Its Applications, IX, *General Electric Rev.*, v. 29, 1926, pp. 274–287.

657. DEARDEN, W. H., and C. BENEDICKS: Magnetic Changes in Iron and Steel below 400°C., *J. Iron Steel Inst.*, v. 113, 1926, pp. 393–417.

658. EDWIN, E.: The Iron Sponge Problem as Solved in Norway with Special Reference to Poor Ores, *Teknisk Tids.* (Bergsvetenskap), v. 56, 1926, pp. 41–52. Abst.: *Chem. Absts.*, v. 20, 1926, p. 2807.

659. EVANS, U. R.: "Corrosion of Metals," E. J. Arnold & Sons, London, 2d ed., 1926, 259 pp.

660. FREEMAN, J. R.: Recrystallization Temperature of Cold-rolled Electrolytic Iron and Open-hearth Steel Strip, *Trans. Am. Soc. Steel Treat.*, v. 10, 1926, pp. 67–86.

661. FUJIHARA, T.: Testing Corrosion of Iron, *Chem. Met. Eng.*, v. 33, 1926, p. 346.

662. FULLER, G. P.: Some Properties of Electrolytic Iron, *Trans. Am. Electrochem. Soc.*, v. 50, 1926, pp. 371–377.

663. GERLACH, W.: Eiseneinkristalle. I: Magnetisierungskurven (Iron Single Crystals. I: Magnetization Curves), *Z. f. Physik*, v. 38, 1926, pp. 828–840.

664. GERLACH, W.: Eiseneinkristalle. II: Magnetisierung, Hysterese und Verfestigung (Iron Single Crystals. II: Magnetization, Hysteresis, and Structure), *Z. f. Physik*, v. 39, 1926, pp. 327–331.

665. HAMPTON, W. H.: Potential of the Iron Electrode, *J. Phys. Chem.*, v. 30, 1926, pp. 980–991.

665A. HAUSSER, K. W., and P. SCHOLZ: Metall-Einkristalle (Single Crystals of Metal), *Wiss. Veröff. Siemens-Konzern*, v. 5, part 3, 1926–1927, pp. 144–164.

666. HEDGES, E. S.: The Periodic Electrochemical Passivity of Iron, Cobalt, Nickel, and Aluminum, *J. Chem. Soc.*, 1926, pp. 2878–2887.

667. HONDA, K., and S. KAYA: On the Magnetization of Single Crystals of Iron, *Sci. Rep.*, Sendai, ser. 1, v. 15, 1926, pp. 721–753.

668. HONDA, K., S. KAYA, and Y. MASUYAMA: On the Magnetic Properties of Single Crystals of Iron, *Nature*, v. 117, 1926, pp. 753–754.

669. HONDA, K., and Y. MASHIYAMA: On the Magnetostriction of Single Crystals of Iron, *Sci. Rep.*, Sendai, ser. 1, v. 15, 1926, pp. 755–776.

670. HÜTTIG, G. F.: Zur Systematik der festen Metall-Wasserstoff Verbindungen (Classification of the Solid Metal-hydrogen Compounds), *Z. angew. Chem.*, v. 39, 1926, pp. 67–75.

670*A*. "International Critical Tables of Numerical Data, Physics, Chemistry and Technology," McGraw-Hill Book Company, Inc., New York, v. 1, 1926, p. 59.

671. ISHIGAKI, T.: On the Change in the Hardness and the Density in Iron and Steel Caused by Cold Working, *Sci. Rep.*, Sendai, ser. 1, v. 15, 1926, pp. 777–794.

672. IWASE, K.: Occlusion of Gases by Metals and Alloys in Liquid and Solid Stages, *Sci. Rep.*, Sendai, ser. 1, v. 15, 1926, pp. 531–566.

673. JORDAN, L., A. A. PETERSON, and L. H. PHELPS: Refractories for Melting Pure Metals: Iron, Nickel, Platinum, *Trans. Am. Electrochem. Soc.*, v. 50, 1926, pp. 155–164.

674. KRIVOBOK, V. N.: A Photomicrographic Study of the Process of Recrystallization in Certain Cold-worked Metals, Paper 1557 *E*, read before Feb. 1926 meeting, Am. Inst. Min. Met. Eng. Abst.: *Chem. Absts.*, v. 20, 1926, p. 3417.

675. LUDWIK, P.: Streckgrenze, Kalt- und Warmsprödigkeit (Yield Strength, Cold and Hot Shortness), *Z. Ver. deutsch. Ing.*, v. 70, 1926, pp. 379–386.

676. MASUMOTO, H.: On a New Transformation of Cobalt and the Equilibrium Diagrams of Nickel-cobalt and Iron-cobalt, *Sci. Rep.*, Sendai, ser. 1, v. 15, 1926, p. 469.

677. McCULLOCH, L.: Passivity and Corrosion of Iron, *Trans. Am. Electrochem. Soc.*, v. 50, 1926, pp. 379–387.

678. MEISSNER, W.: Messungen mit Hilfe von flüssigem Helium. II. Widerstand von Gold, Zink, Cadmium, Platin, Nickel, Eisen und Silber bis herab zu 1.3° Abs. (Measurements Employing Liquid Helium. II. Resistance of Gold, Zinc, Cadmium, Platinum, Nickel, Iron, and Silver Down to 1.3° Abs.), *Z. f. Physik*, v. 38, 1926, pp. 647–658.

679. MONK, R. H., and R. J. TRAILL: Electrolytic Iron from Ilmenite Ores, *Can. Chem. Met.*, v. 10, 1926, pp. 137–159.

680. OSAWA, A.: On the Relation between the Lattice Constant and the Density of Iron-nickel Alloys, *J. Iron Steel Inst.*, v. 113, 1926, pp. 447–456.

681. PFEIL, L. B.: The Deformation of Iron, with Particular Reference to Single Crystals, *Iron Steel Inst., Carn. Schol. Mem.*, v. 15, 1926, pp. 319–380.

682. PFEIL, L. B.: The Effect of Occluded Hydrogen on the Tensile Strength of Iron, *Proc. Royal Soc.* (London), ser. A, v. 112, 1926, pp. 182–195.

683. RAWDON, H. S., P. HIDNERT, and W. A. TUCKER: Some Effects of Hydrogen on Iron and Their Bearing on a Reported Transformation at 370° Cent. (698° Fahr.), *Trans. Am. Soc. Steel Treat.*, v. 10, 1926, pp. 233–256.

684. RIBBECK, F.: Über die Abhängigkeit des elektrischen Widerstandes der Nickelstähle von Zusammensetzung, Temperatur und Wärmebehandlung (The Influence of Composition, Temperature, and Heat Treatment on the Electric Resistance of Nickel Steel), *Z. f. Physik*, v. 38, 1926, pp. 772–787; 887–907; v. 39, 1926, pp. 787–812.

685. ROHN, W.: Säurefeste Legierungen mit Nickel als Basis (Nickel-base Acid-resistant Alloys), *Z. f. Metallkunde*, v. 18, 1926, pp. 387–396.

686. SPELLER, F. N.: "Corrosion, Causes and Prevention," McGraw-Hill Book Company, Inc., New York, 1926, 621 pp.

687. SYKES, W. P.: The Iron-molybdenum System, *Trans. Am. Soc. Steel Treat.*, v. 10, 1926, pp. 839–869.

688. SYKES, W. P.: The Iron-tungsten System, *Trans. Am. Inst. Min. Met. Eng.*, v. 73, 1926, pp. 968–1008.

689. TAYLOR, G. I., and C. F. ELAM: The Distortion of Iron Crystals, *Proc. Royal Soc.* (London), ser. A, 112, 1926, pp. 337–361.

690. THOMPSON, J. G.: Resistance of Metals to Nitric Acid, *Chem. Met. Eng.*, v. 33, 1926, pp. 614–616.

691. TRAILL, R. J., and W. R. McCLELLAND: Process for the Treatment of Ilmenite for the Recovery of Electrolytic Iron and Titanium Oxide Concentrates, *Can. Dept. Mines, Mines Br. Rep.* 688, 1926, pp. 96–101.

692. TRAILL, R. J., and W. R. McCLELLAND: Process for the Hydrometallurgical Treatment of High Copper Iron Sulphide Concentrates with Recovery of Iron by Electrolysis, *Can. Dept. Mines, Mines Br. Rep.* 688, 1926, pp. 101–109.

693. UMINO, S.: On the Specific Heat of Carbon Steels, *Sci. Rep.*, Sendai, ser. 1, v. 15, 1926, pp. 331–369.

694. UMINO, S.: On the Latent Heat of Fusion of Several Metals and Their Specific Heats at High Temperatures, *Sci. Rep.*, Sendai, ser. 1, v. 15, 1926, pp. 597–617.

695. WEBSTER, W. L.: The Longitudinal Magneto-resistance Effect in Single Crystals of Iron, *Proc. Royal Soc.* (London), ser. A, v. 113, 1926–1927, pp. 196–207.

696. YAMADA, Y.: On the Solubility of Carbon in Pure Iron, *Sci. Rep.*, Sendai, ser. 1, v. 15, 1926, pp. 851–855.

1927

697. ANON.: Eliminating Blast Furnace in Norway, *Iron Age*, v. 119, 1927, pp. 562–565.

698. ANON.: Making Sponge Iron in Japan, *Iron Age*, v. 120, 1927, pp. 937–938.

699. BAGDASARIAN, A. B.: Reduction of Metallic Chlorides by Hydrogen, *Trans. Am. Electrochem. Soc.*, v. 51, 1927, pp. 449–494.

700. BANCROFT, W. D.: Twenty-five Years of Theoretical Electrochemistry, *Trans. Am. Electrochem. Soc.*, v. 51, 1927, pp. 25–40.

701. BORELIUS, G.: Löslichkeit und Diffusion von Wasserstoff in Metallen (Solubility and Diffusion of Hydrogen in Metals), *Ann. d. Physik*, ser. 4, v. 83, 1927, pp. 121–136.

702. CHEVENARD, P.: Recherches expérimentales sur les alliages de fer, de nickel et de chrome (Alloys of Iron, Nickel, and Chromium), *Travaux et Mém. Bur. Int. Poids et Mesures*, v. 17, 1927, (2), pp. 59–61.

703. CROSS, H. C., and E. E. HILL: Density of Hot-rolled and Heat-treated Carbon Steels, *National Bur. Stds. Sci. Papers*, v. 22, 1927–1928, pp. 451–466.

704. CZOCHRALSKI, J.: Geschichtlicher Beitrag zur Frage der Rekristallisation (Historical Contribution to the Problem of Recrystallization), *Z. f. Metallkunde*, v. 19, 1927, pp. 316–320.

705. DESCH, C. H.: Equilibrium Diagrams, Ferrous Alloys, *International Critical Tables*, v. 2, 1927, p. 451.

706. DUSSLER, E., and W. GERLACH: Eiseneinkristalle. III. Die Magnetisierung in verschiedenen Kristallrichtungen (Single Iron Crystals, III. Magnetization in Different Crystal Directions), *Z. f. Physik*, v. 44, 1927, pp. 279–285.

707. EICHENBERG, G., and W. OERTEL: Über den Einfluss der Behandlung des Transformatoreneisens auf seine Wattverluste (The Influence of Treatment of Transformer Iron on Watt Losses), *Stahl u. Eisen*, v. 47, 1927, pp. 262–271.

708. EILENDER, W., and W. OERTEL: Der Einfluss des Sauerstoffs auf die Eigenschaften des Stahles (Influence of Oxygen on the Properties of Steel), *Stahl u. Eisen*, v. 47, 1927, pp. 1558–1561.

709. ESSER, H.: Dilatometrische und magnetische Untersuchungen an reinem Eisen und Eisen-Kohlenstoff-Legierungen (Dilatometric and Magnetic Investigation of Pure Iron and Iron-carbon Alloys), *Stahl u. Eisen*, v. 47, 1927, pp. 337–344.

710. EUCKEN, A., and K. DITTRICH: Zur Kenntnis des Wiedemann-Franzschen Gesetzes, II. (A Study of the Wiedemann-Franz Law, II), *Z. phys. Chem.*, v. 125, 1927, pp. 211–228.

711. EVANS, U. R.: The Passivity of Metals, *J. Chem. Soc.*, 1927, pp. 1020–1040.

712. FREUNDLICH, H., G. PATSCHEKE, and H. ZOCHER: Über die Passivität von Eisenspiegeln (Passivity of Iron Mirrors), *Z. phys. Chem.*, v. 128, 1927, pp. 321–344; v. 130, 1927, pp. 289–307.

713. FRIEND, J. N.: Third Report on the Relative Corrodibilities of Various Commercial Forms of Iron and Steel, *Iron Steel Inst., Carn. Schol. Mem.*, v. 16, 1927, pp. 131–151.

714. GOUGH, H. J.: Fatigue Phenomena with Special Reference to Single Crystals, *J. Royal Soc. Arts*, v. 76, 1927–1928, pp. 1025–1044; 1045–1062; 1065–1081; 1085–1142.

715. GROEBLER, H., and P. OBERHOFFER: Beiträge zur Untersuchung der Oxyde des Eisens, besonders des Eisenoxyduls (Investigation of the Oxides of Iron, Especially Ferrous Oxide), *Stahl u. Eisen*, v. 47, 1927, pp. 1984–1988.

716. GRÜNEISEN, E., and E. GOENS: Untersuchungen an Metallkristallen. V. Elektrizitäts- und Wärmeleitung von ein- und vielkristallinen Metallen des regulären Systems (Studies of Metal Crystals. V.

Electric and Thermal Conductivity of Single Crystals and Poly-crystalline Metals of the Regular System), *Z. f. Physik*, v. 44, 1927, pp. 615–642.

717. HALVORSON, H. O., and R. L. STARKEY: Studies on the Transformation of Iron in Nature, *J. Phys. Chem.*, v. 31, 1927, pp. 626–631.

718. HAUGHTON, J. L.: Alloys of Iron Research, VIII. The Constitution of Alloys of Iron and Phosphorus, *J. Iron Steel Inst.*, v. 115, 1927, pp. 417–433.

719. HERTY, C. H., JR., J. M. GAINES, JR., B. M. LARSEN, W. A. SIMKINS, R. L. GERUSO, and S. P. WATKINS: The Physical Chemistry of Steel Making: The Solubility of Iron Oxide in Iron, *Cooperative Bull.* 34, Min. Met. Advisory Boards to Carnegie Inst. Tech. and U. S. Bur. Mines, Pittsburgh, 1927, 69 pp.

720. HODSON, F., and O. SMALLEY: Developments in the Low-temperature Reduction of Iron Ore, *Trans. Am. Electrochem. Soc.*, v. 51, 1927, pp. 225–243.

721. HONDA, K., and H. ENDO: On the Volume Change in Cast Iron during Solidification, with a Criticism of the Double Diagram of the Iron-carbon System, *Sci. Rep.*, Sendai, ser. 1, v. 16, 1927, pp. 9–25.

722. HONDA, K., and H. ENDO: On the Magnetic Susceptibility of the Iron-carbon Alloys at High Temperatures, and the Equilibrium Diagram of the System, *Sci. Rep.*, Sendai, ser. 1, v. 16, 1927, pp. 627–637.

723. JOHNSTON, T.: Electrodeposition of Iron, *Metal Industry* (London), v. 30, 1927, pp. 241–242; 293–294.

724. JONES, H. A., I. LANGMUIR, and G. M. J. MACKAY: The Rates of Evaporation and the Vapor Pressures of Tungsten, Molybdenum, Platinum, Nickel, Iron, Copper, and Silver, *Phys. Rev.*, v. 30, 1927, pp. 201–214.

725. KLINKHARDT, H.: Messung von wahren spezifischen Wärmen bei hohen Temperaturen durch Heizung mit Glühelektronen (Measurement of True Specific Heats at High Temperatures by Heating with Thermionic Electrons), *Ann. d. Physik*, ser. 4, v. 84, 1927, pp. 167–200.

726. DELANGERON, N. A.: Fabrication, propriétés et emploi du fercarbonyle (Manufacture, Properties, and Uses of Iron-carbonyl), *Rev. univ. des Mines*, ser. 7, v. 16, 1927, pp. 145–161.

727. LOMBARD, V.: Perméabilité du fer et du platine à l'hydrogène (Permeability of Iron and Platinum to Hydrogen), *C. R. Acad. Sci.*, Paris, v. 184, 1927, pp. 1557–1559.

728. LONGMUIR, P.: The Direct Production of Pure Iron, *Trans. Am. Electrochem. Soc.*, v. 51, 1927, pp. 267–278.

729. MANTELL, C. L., and W. G. KING, JR.: Reversed Potentials in the Corrosion of Tin Plate, *Trans. Am. Electrochem. Soc.*, v. 52, 1927, pp. 435–441.

730. MASING, G., and L. KOCH: Duraluminartige Vergütung bei Eisen-Kohlenstoff-Legierungen (The Duralumin Type of Treatment of

Iron-carbon Alloys), *Wiss. Veröff. Siemens-Konzern*, v. 6, 1927–1928, pp. 202–210.

731. McADAM, D. J., JR.: Fatigue and Corrosion Fatigue of Metals, *Intern. Congress Test. Mat.*, (1), Amsterdam, Holland, 1927, pp. 305–358.

732. McKEEHAN, L. W.: Iron Crystals, *Nature*, v. 119, 1927, pp. 705–706.

733. OBERHOFFER, P.: Entwicklung und Stand der Qualitätsfrage (Development and Status of the Question of Quality), *Stahl u. Eisen*, v. 47, 1927, p. 1521.

734. OBERHOFFER, P., and H. ESSER: Zur Kenntnis des Zustandsdiagramms Eisen-Chrom (The Iron-chromium Diagram), *Stahl u. Eisen*, v. 47, 1927, pp. 2021–2031.

735. OBERHOFFER, P., and W. GROSSE: Die spezifische Wärme des Eisens (Specific Heat of Iron), *Stahl u. Eisen*, v. 47, 1927, pp. 576–582.

736. PFEIL, L. B.: The Effect of Cold Work on the Structure and Hardness of Single Iron Crystals and the Changes Produced by Subsequent Annealing, *Iron Steel Inst., Carn. Schol. Mem.*, v. 16, 1927, pp. 153–210.

737. POMP, A., and A. DAHMEN: Entwicklung eines abgekürzten Prüfverfahrens zur Ermittlung der Dauerstandfestigkeit von Stahl bei erhöhten Temperaturen (Development of an Accelerated Testing Method for Determining the Tensile Strength under Prolonged Loading of Steel at Elevated Temperatures), *Mitt. K.-W. Inst. Eisenforschung*, v. 9, 1927, pp. 33–52.

738. RAWDON, H. S., and T. BERGLUND: Unusual Features in the Microstructure of Ferrite, *National Bur. Stds. Sci. Papers*, v. 22, 1927–1928, pp. 649–717.

739. SCHENCK, R., and T. DINGMANN: Gleichgewichtsuntersuchungen über die Reduktions-, Oxydations-, und Kohlungsvorgänge beim Eisen. III. (Equilibrium Relations in the Reduction, Oxidation, and Carburization of Iron. III), *Z. anorg. allgem. Chem.*, v. 166, 1927, pp. 113–154.

740. SCHULZE, A.: Zur Konstitution der Kobalt-Nickel- und Kobalt-Eisenlegierungen (Constitution of Cobalt-nickel and Cobalt-iron Alloys), *Z. tech. Physik*, v. 8, 1927, pp. 423–427.

741. TAMMANN, G., and W. SALGE: Zur Bestimmung der Temperatur des Beginns der Rekristallisation (Determination of the Temperature of the Commencement of Recrystallization), *Z. f. Metallkunde*, v. 19, 1927, pp. 187–188.

742. TAPSELL, H. J., and W. J. CLENSHAW: Properties of Materials at High Temperatures, *Dept. Sci. Ind. Research, Eng. Res., Special Rep.* 1, 1927, 60 pp.

743. TRITTON, F. S.: Some Unusual Microstructures in Iron, *Metallurgist*, v. 3, 1927, pp. 88–90.

744. TUYN, W., and H. K. ONNES: Nouvelles mesures relatives à la résistance électrique des métaux aux températures de l'hélium liquide (New Measurements of the Electric Resistance of Metals

at the Temperature of Liquid Helium), *Arch. Néerlandaises des Sciences*, ser. 3*A*, v. 10, 1927, pp. 5–41.

745. UMINO, S.: On the Heat of the A_2 and A_3 Transformations in Carbon Steels, *Sci. Rep.*, Sendai, ser. 1, v. 16, 1927, pp. 1009–1030.

746. VAN ARKEL, A. E., and P. KOETS: Das Wesen der Rekristallisationskerne bei Metallen (The Nature of the Recrystallization Nuclei in Metals), *Z. f. Physik*, v. 41, 1927, pp. 701–707.

747. VANICK, J. S., W. W. DE SVESHNIKOFF, and J. G. THOMPSON: Deterioration of Steels in the Synthesis of Ammonia, *National Bur. Stds. Tech. Papers*, v. 22, 1927–1928, pp. 199–233.

748. VERNON, W. H. J.: Second Experimental Report to the Atmospheric Corrosion Research Committee (British Non-Ferrous Metals Research Association), *J. Inst. Metals*, v. 38, 1927, pp. 443*A*–444*A*.

749. WEBSTER, W. L.: The Transverse Magneto-resistance Effect in Single Crystals of Iron, *Proc. Royal Soc.* (London), ser. A, v. 114, 1927, pp. 611–619.

750. WEVER, F.: Über die Natur der magnetischen Umwandlung des Eisens (The Nature of the Magnetic Transformation in Iron), *Z. anorg. allgem. Chem.*, v. 162, 1927, pp. 193–202.

751. WHITELEY, J. H.: The Solution of Cementite in Alpha Iron and its Precipitation, *J. Iron Steel Inst.*, v. 116, 1927, pp. 293–303.

752. WIBERG, M.: A New Method for the Production of Iron Sponge, *Trans. Am. Electrochem. Soc.*, v. 51, 1927, pp. 279–304.

753. WILLIAMS, C. E., E. P. BARRETT, and B. M. LARSEN: Production of Sponge Iron, *U. S. Bur. Mines Bull.* 270, 1927, 175 pp.

754. WINKELMANN, A.: Über die Einwirkung verschiedener Metalle auf Lösungen von Beizmitteln (The Action of Various Metals on Solutions of Fungicides), *Z. angew. Chem.*, v. 40, 1927, pp. 1393–1394.

755. WÜST, F.: Die direkte Erzeugung des Eisens (The Direct Production of Iron), *Stahl u Eisen*, v. 47, 1927, pp. 905–915; 955–965.

1928

756. AKULOV, N.: Die Magnetostriktion des Eiseneinkristalls (Magnetostriction of the Single Crystal of Iron), *Z. f. Physik*, v. 52, 1928–1929, pp. 389–405.

757. ANON.: Electrolytic Iron, *Foundry Tr. J.*, v. 38, 1928, p. 118.

758. ANON.: New Direct Steel Process of W. H. Smith, *Iron Age*, v. 122, 1928, p. 1543.

759. ANON.: Making Iron Sponge from Ferrous Sand in Japan, *Foundry Tr. J.*, v. 38, 1928, p. 64.

760. ANON.: Electrolytic Iron: Its Inception and Development, *Engineering*, v. 125, 1928, pp. 339–340.

761. ARNFELT, H.: On the Constitution of the Iron-tungsten and the Iron-molybdenum Alloys, *Iron Steel Inst., Carn. Schol. Mem.*, v. 17, 1928, pp. 1–21.

762. AUWERS, O. VON: Über Kristallstruktur und Ferromagnetismus (Crystal Structure and Ferromagnetism), *Physik. Z.*, v. 29, 1928, pp. 921–927.

763. AUWERS, O. VON: Über den Einfluss der Korngrösse auf die magnetischen Eigenschaften des Eisens (The Influence of Grain Size on the Magnetic Properties of Iron), *Z. tech. Physik*, v. 9, 1928, pp. 475–478; discussion *ibid.*: v. 10, 1929, pp. 67–68. Also: *Wiss. Veröff. Siemens-Konzern*, v. 7, 1928–1929, pp. 197–209.

764. BARDENHEUER, P., and H. SCHMIDT: Der Einfluss der Kaltverformung und der Wärmebehandlung auf die elektrische Leitfähigkeit von Kupfer, Aluminium und Eisen (The Effect of Cold Work and Heat Treatment on the Electric Conductance of Copper, Aluminum, and Iron), *Mitt. K.-W. Inst. Eisenforschung*, v. 10. 1928, pp. 193–212.

765. BENEDICKS, C., and H. LÖFQUIST: Zur Frage der Löslichkeit des Sauerstoffs in Eisen, bzw. in Eisenoxydul (The Question of the Solubility of Oxygen in Iron or Ferrous Oxide), *Z. anorg. allgem. Chem.*, v. 171, 1928, pp. 231–238.

766. BOYLSTON, H. M.: "Iron and Steel," John Wiley & Sons, New York, 1928, pp. 323–334.

767. BRACE, P. H., and N. A. ZIEGLER: Application of a High Vacuum Induction Furnace to the Study of Gases in Metals, *Trans. Am. Inst. Min. Met. Eng.*, v. 78, 1928, pp. 544–564.

768. BRILL, R., and H. MARK: Röntgenographische Studien am Abbau komplexer Eisencyanide (Röntgenographic Study of the Decomposition of Complex Iron Cyanides), *Z. phys. Chem.*, v. 133, 1928, pp. 443–458.

769. BROWN, H. M.: Effect of Magnetic Fields upon Thermal Conductivity of Iron, Copper, Gold, Silver, and Zinc, *Phys. Rev.*, v. 32, 1928, pp. 508–514.

770. DEHLINGER, U.: Die Rekristallisation der Metalle (Recrystallization of Metals), *Metallwirtschaft*, v. 7, 1928, pp. 1172–1176. Abst.: *Chem. Absts.*, v. 23, 1929, p. 2680.

771. DUSSLER, E.: Eiseneinkristalle. IV. Die Temperaturabhängigkeit der Magnetisierung von Eiseneinkristallen (Single Iron Crystals. IV. The Effect of Temperature on the Magnetization of Single Iron Crystals), *Z. f. Physik*, v. 50, 1928, pp. 195–214.

772. EBERT, H.: Ausdehnungsmessungen bei tiefen Temperaturen (Expansion Measurements at Low Temperatures), *Z. f. Physik*, v. 47, 1928, pp. 712–722.

773. EISENHUT, O., and E. KAUPP: Röntgenographische Untersuchungen über Eisenkatalysatoren für die Ammoniaksynthese (Röntgenographic Investigation of Iron Catalysts for Ammonia Synthesis), *Z. phys. Chem.*, v. 133, 1928, pp. 456–471.

774. ENDO, H.: On the Corrosion of Iron, *Sci. Rep.*, Sendai, ser. 1, v. 17, 1928, pp. 1111–1134.

775. ENDO, H.: The Corrosion of Steel by Acid Solutions, *Sci. Rep.*, Sendai, ser. 1, v. 17, 1928, pp. 1245–1263.

776. ENDO, H.: The Effect of Cold Working on the Corrosion of Iron and Steel, *Sci. Rep.*, Sendai, ser. 1, v. 17, 1928, pp. 1265–1278.

777. EVANS, U. R.: The Practical Problems of Corrosion, Part III. The Formation of Rust and its Consequences, *J. Soc. Chem. Ind.*, v. 47 T, 1928, pp. 55–62.

778. EVANS, U. R.: The Practical Problems of Corrosion, Part V. Corrosion and Protection at the Contacts of Dissimilar Metals, *J. Soc. Chem. Ind.*, v. 47 T, 1928, pp. 73–77.

779. FRIEND, J. N.: The Relative Corrodibilities of Ferrous and Non-ferrous Metals and Alloys, Part I, *J. Inst. Metals*, v. 39, 1928, pp. 111–133.

780. GOUGH, H. J.: The Behavior of a Single Crystal of Alpha Iron Subjected to Alternating Torsional Stresses, *Proc. Royal Soc.* (London), ser. A, v. 118, 1928, pp. 498–534.

781. GRIES, H., and H. ESSER: Über Einkristalle aus Eisen (Single Crystals of Iron), *Archiv f. d. Eisenhüttenwesen*, v. 2, 1928–1929, pp. 749–761.

782. GUERTLER, W., and W. ACKERMANN: Einige Versuche über Säurebeständigkeit reinster Chrom-Nickel-Eisenlegierungen (Investigations of the Acid Resistance of Pure Chromium-nickel-iron Alloys), *Z. f. Metallkunde*, v. 20, 1928, pp. 269–279.

783. HONDA, K., H. MASUMOTO, and S. KAYA: On the Magnetization of Single Crystals of Iron at High Temperatures, *Sci. Rep.*, Sendai, ser. 1, v. 17, 1928, pp. 111–130.

784. HONDA, K., and S. MIURA: On the Determination of the Heterogeneous Field in the Iron-nickel System, *Trans. Am. Soc. Steel Treat.*, v. 13, 1928, pp. 270–279.

785. IWASE, K., and K. MIYAZAKI: On the Electrode Potential of Single Crystals of Iron, *Sci. Rep.*, Sendai, ser. 1, v. 17, 1928, pp. 163–167.

786. KAYA, S.: Densities of Single Crystals of Iron, Nickel, and Aluminum, *Kinzoku no Kenkyu* (*J. Study Metals*), v. 5, 1928, pp. 385–386 (in Japanese). Abst.: *Chem. Absts.*, v. 23, 1929, p. 2339.

787. KENYON, R. L.: Armco Ingot Iron, *Trans. Am. Soc. Steel Treat.*, v. 13, 1928, pp. 240–269; 435–464.

788. KINZEL, A. B.: Critical Points in Chromium-iron Alloys, *Trans. Am. Inst. Min. Met. Eng.*, v. 80, 1928, p. 301–307.

789. KNOWLTON, L. G.: Some Experiments on Iron, *J. Phys. Chem.*, v. 32, 1928, pp. 1572–1595.

790. KOHMAN, E. F., and N. H. SANBORN: Tin Plate and the Electrochemical Series, *J. Ind. Eng. Chem.*, v. 20, 1928, pp. 76–79.

791. KOHMAN, E. F., and N. H. SANBORN: Factors Affecting the Relative Potentials of Tin and Iron, *J. Ind. Eng. Chem.*, v. 20, 1928, pp. 1373–1377.

792. KÖRBER, F., and H. HOFF: Über die Festigkeitseigenschaften und den Reisswinkel kaltgewalzter Metalle (The Strength and Tearing Angle of Cold-rolled Metals), *Mitt. K.-W. Inst. Eisenforschung*, v. 10, 1928, pp. 175–187.

793. LATTRE, G. DE: Le Cadmiumage (Cadmium-coating Method), *Rev. de Mét.*, *Mém.* v. 25, 1928, pp. 630–636.

794. LOGAN, K. H., S. P. EWING, and C. D. YOEMANS: Bureau of Standards Soil Corrosion Studies, I, *National Bur. Stds. Tech. Papers*, v. 22, 1928, pp. 447–554.

795. LUECK, R. H., and H. T. BLAIR: Tin Plate and the Electrochemical Series, *J. Ind. Eng. Chem.*, v. 20, 1928, pp. 443–444.

796. MITTASCH, A.: Über Eisencarbonyl und Carbonyleisen (Iron Carbonyl and Carbonyl Iron), *Z. angew. Chem.*, v. 41, 1928, pp. 827–833.

797. MIYAZAKI, K.: The Equilibrium Diagram of the Iron and Iron Sulphide System, *Sci. Rep.*, Sendai, ser. 1, v. 17, 1928, pp. 877–881.

798. MÜLLER, W. J.: Neue Untersuchungen zur Passivität der Metalle (New Investigations on Passivity of Metals), *Z. f. Elektrochemie*, v. 34, 1928, pp. 571–586.

799. NEUENDORFF, G., and F. SAUERWALD: Über die Gewinnung der Schwermetalle durch Schmelzelektrolyse (Production of Heavy Metals from Fused Electrolytes), *Z. f. Elektrochemie*, v. 34, 1928, pp. 199–204.

800. OBERHOFFER, P., and C. KREUTZER: Beiträge zu den Systemen Eisen-Silizium, Eisen-Chrom und Eisen-Phosphor (Contribution to the Systems Iron-silicon, Iron-chromium, and Iron-phosphorus), *Archiv f. d. Eisenhüttenwesen*, v. 2, 1928–1929, pp. 449–456.

801. PFEIL, L. B.: The Change in Tensile Strength Due to Aging of Cold Drawn Iron and Steel, *J. Iron Steel Inst.*, v. 118, 1928, pp. 167–181.

802. RAWDON, H. S.: "Protective Metal Coatings," The Chemical Catalog Co., Inc., New York, 1928, 277 pp.

803. RUER, R., and J. KUSCHMANN: Über die Reduktion des durch Wägung in Luft ermittelten Gewichtes pulverförmiger Substanzen auf den leeren Raum (Reduction of the Weights of Powdered Substances Weighed in Air to Weights "in Vacuo"), *Z. anorg. allgem. Chem.*, v. 173, 1928, pp. 233–261.

804. RUF, K.: Einige physikalische Konstanten von reinen kohlefreien Chrom-Eisen- und Vanadium-Eisen-Legierungen (Some Physical Constants of Pure Carbon-free Chromium-iron and Vanadium-iron Alloys), *Z. f. Elektrochemie*, v. 34, 1928, pp. 813–818.

805. SCHULZE, A.: Die Magnetostriktion (Magnetostriction), *Z. f. Physik*, v. 50, 1928, pp. 448–505.

806. SIZOO, G. J.: Über den Zusammenhang zwischen Korngrösse und magnetischen Eigenschaften bei reinem Eisen (The Relation between Grain Size and Magnetic Properties of Pure Iron), *Z. f. Physik*, v. 51, 1928, pp. 557–564.

807. TAMMANN, G., and J. SCHNEIDER: Zur Kenntnis der Abhängigkeit der Absorptionsgeschwindigkeit des Wasserstoffes durch Pd, Fe und Ni von der Kristallitenorientierung (The Relationship between Crystal Orientation and the Rate of Absorption of Hydrogen by Palladium, Iron, and Nickel), *Z. anorg. allgem. Chem.*, v. 172, 1928, pp. 43–64.

808. VAN LIEMPT, J. A. M.: Production of Metallic Single Crystals, *Trans. Am. Inst. Min. Met. Eng.*, v. 78, 1928, pp. 307–314.

809. VERNON, W. H. J.: "A Bibliography of Metallic Corrosion," Edward Arnold and Co., London, 1928, 341 pp.

810. WEVER, F.: Über den Einfluss der Elemente auf den Polymorphismus des Eisens (The Influence of the Elements on the Polymorphism of Iron), *Archiv f. d. Eisenhüttenwesen*, v. 2, 1928–1929, pp. 739–746.

811. WILLEY, E. J. B.: On Active Nitrogen. Part VI. The Formation of Iron Nitride in the Iron-nitrogen Arc, *J. Chem. Soc.*, 1928, pp. 2840–2844.

812. WOHRMAN, C. R.: Inclusions in Iron, *Trans. Am. Soc. Steel Treat.*, v. 14, 1928, pp. 255–299.

813. YENSEN, T. D.: What is the Magnetic Permeability of Iron? *J. Franklin Inst.*, v. 206, 1928, pp. 503–510.

1929

814. AMMERMANN, E., and H. KORNFELD: Über den Zusammenhang zwischen α-Aederung und A_3-Umwandlung (The Relation between Alpha Veining and the A_3 Transformation), *Archiv f. d. Eisenhüttenwesen*, v. 3, 1929–1930, pp. 307–311. Abst.: *Metals & Alloys*, v. 1, 1929–1930, pp. 334–335.

815. ANDREW, J. H., and D. BINNIE: The Liquidus and Solidus Ranges of Some Commercial Steels, *J. Iron Steel Inst.*, v. 119, 1929, pp. 309–346.

816. BACH, R.: Contribution à l'étude roentgenographique de l'état crystallin du fer (Roentgenographic Study of the Crystalline State of Iron), *Helv. Phys. Acta*, v. 2, 1929, pp. 95–114.

817. BENEDICKS, C., N. ERICSSON, and G. ERICSON: Bestimmung des spezifischen Volumens von Eisen, Nickel und Eisenlegierungen im geschmolzenen Zustand (Determination of the Specific Volume of Iron, Nickel, and Iron Alloys in the Molten State), *Archiv f. d. Eisenhüttenwesen*, v. 3, 1929–1930, pp. 473–486.

818. DEAN, R. S., R. O. DAY, and J. L. GREGG: Relation of Nitrogen to Blue Heat Phenomena in Iron and Dispersion Hardening in the System Iron-nitrogen, *Trans. Am. Inst. Min. Met. Eng.*, v. 84, 1929, pp. 446–453.

819. DEHLINGER, U.: Zur Theorie der Rekristallisation reiner Metalle (Theory of Recrystallization of Pure Metals), *Ann. d. Physik*, ser. 5, v. 2, 1929, pp. 749–793.

820. DICKIE, H. A.: The Solubility of Carbide in Ferrite, *J. Iron Steel Inst.*, v. 120, 1929, pp. 161–185.

821. EILENDER, W., and R. WASMUHT: Ein Beitrag zur Frage der Ausscheidungshärtung des Eisens (The Precipitation Hardening of Iron), *Archiv f. d. Eisenhüttenwesen*, v. 3, 1929–1930, pp. 659–664. Extract: *Metals & Alloys*, v. 1, 1929–1930, pp. 732–735.

822. EPSTEIN, S., H. C. CROSS, E. C. GROESBECK, and I. J. WYMAN: Observations on the Iron-nitrogen System, *National Bur. Stds. J. Res.*, v. 3, 1929, pp. 1005–1027. Also: *Trans. Am. Soc. Steel Treat.*, Nitriding Symposium, v. 16, 1929, pp. 19–58.

823. EVANS, U. R.: The Passivity of Metals and Its Relation to Problems of Corrosion, *Trans. Am. Inst. Min. Met. Eng.*, v. 83, 1929, pp. 7–28.

824. EVANS, U. R.: The Passivity of Metals.   Part 2.   The Breakdown of the Protective Film and the Origin of Corrosion Currents, *J. Chem. Soc.*, 1929, pp. 92–110.

825. EVANS, U. R.: The Mechanism of Corrosion, *J. Chem. Soc.*, 1929, pp. 111–129.

826. EVANS; U. R.: The Passivity of Metals.   Part 3.   The Quantity and Distribution of the Superficial Oxide, *J. Chem. Soc.*, 1929, pp. 2651–2660.

826*A*. FAIRCHILD, C. O., W. H. HOOVER, and M. F. PETERS: A New Determination of the Melting Point of Palladium, *National Bur. Stds. J. Res.*, v. 2, 1929, pp. 931–962.

827. FINK, C. G., and C. M. DeCROLY: The Corrosion Rate of Ferronickel Alloys, *Trans. Am. Electrochem. Soc.*, v. 56, 1929, pp. 239–273.

828. FRIEND, J. N.: The Relative Corrodibilities of Ferrous and Nonferrous Metals and Alloys.   Part II, *J. Inst. Metals*, v. 42, 1929, pp. 149–152.

829. GILLETT, H. W.: Discussion of paper by M. A. Grossmann, On Oxygen Dissolved in Steel, and Its Influence on the Structure, *Trans. Am. Soc. Steel Treat.*, v. 16, 1929, pp. 29–39.

830. GRAY, H. H., and M. B. THOMPSON: The Influence of Nitrogen on the Solubility of Ferrous Materials in Hydrochloric Acid, *J. Soc. Chem. Ind.*, v. 48, 1929, pp. 21T-28T.

831. GRIES, H., and H. ESSER: Magnetische Messungen an Eisenviel- und Eiseneinkristallen mit einem neuartigen magnetischen Spannungsmesser (Magnetic Measurements on Polycrystalline and Single-crystal Iron with a New Magnetic Potentiometer), *Arch. f. Elektrotechnik*, v. 22, 1929, pp. 145–152.

832. GROSSMANN, M. A.: On Oxygen Dissolved in Steel, and Its Influence on the Structure, *Trans. Am. Soc. Steel Treat.*, v. 16, 1929, pp. 1–19.

833. HICKS, J. F. G.: Observations on the Corrosion of Iron, *J. Phys. Chem.*, v. 33, 1929, pp. 780–790.

834. "International Critical Tables of Numerical Data, Physics, Chemistry and Technology," McGraw-Hill Book Company, Inc., New York, vols. 5 and 6, 1929, 470 and 471 pp.

835. JAQUEROD, A., and S. GAGNEBIN: Sur un point singulier du fer (A Singular Point in Iron), *Helv. Phys. Acta*, v. 2, 1929, pp. 156–158.

836. KANGRO, W., and R. FLÜGGE: Über die Einwirkung von Chlor auf Eisenoxyde (The Action of Chlorine on Iron Oxide), *Z. f. Elektrochemie*, v. 35, 1929, pp. 189–194.

837. KÖSTER, W.: Über die Eigenschaftsänderungen der Eisen-Stickstoff-Legierungen durch Abschrecken und Anlassen unterhalb A_1 (The Effect of Quenching and Tempering below the A_1 Point upon the Properties of Iron-nitrogen Alloys), *Archiv f. d. Eisenhüttenwesen*, v. 3, 1929–1930, pp. 553–558.   Also: *Metals & Alloys*, v. 1, 1929–1930, pp. 571–575.

838. KÖSTER, W.: Zur Frage des Stickstoffs im technischen Eisen (The Problem of Nitrogen in Commercial Iron), *Archiv f. d. Eisenhüttenwesen*, v. 3, 1929–1930, pp. 637–655.

839. KRINGS, W., and J. KEMPKENS: Über die Löslichkeit des Sauerstoffs im festen Eisen (The Solubility of Oxygen in Solid Iron), *Z. anorg. allgem. Chem.*, v. 183, 1929, pp. 225–250.

840. KROLL, W.: Die Legierungen des Berylliums mit Eisen (The Alloys of Beryllium with Iron), *Wiss. Veröff. Siemens-Konzern*, v. 8, 1929, pp. 220–235. Also: RIMBACH, R., and A. J. MICHEL (translators): "Beryllium, Its Production and Application," The Chemical Catalog Co., New York, 1932, 331 pp.

841. KUTTER, F.: Über das Verhalten einiger Metalle gegen Würze und Bier (The Action of Metals on Wort and Beer), *Z. ges. Brauwesen*, v. 52, 1929, pp. 13–20; 27–34. Abst.: *J. Inst. Brewing*, v. 35, 1929, p. 210. Abst.: *J. Inst. Metals*, v. 41, 1929, p. 488*A*.

842. LLOYD, S. J.: Alkaline Electrolytic Iron, *Trans. Am. Electrochem. Soc.*, v. 55, 1929, pp. 305–314.

843. LOGAN, K. H.: Soil Corrosion Studies 1927–1928, *National Bur. Stds. J. Res.*, v. 3, 1929, pp. 275–302.

844. MARTIN, E.: Ein Beitrag zur Frage der Aufnahmefähigkeit des reinen Eisens und einiger seiner Legierungselemente für Wasserstoff und Stickstoff (The Absorptive Power of Pure Iron and Some of Its Alloying Elements for Hydrogen and Nitrogen), *Archiv f. d. Eisenhüttenwesen*, v. 3, 1929–1930, pp. 407–416.

845. MAYER, G.: Die Gitter-Konstante von reinem Alpha-Eisen (The Lattice Constant of Pure Alpha Iron), *Z. f. Kristallographie*, v. 70, 1929, pp. 383–384.

846. MCAULAY, A. L., and S. H. BASTOW: The Electrical Behavior of Surfaces of Corroding Iron, *J. Chem. Soc.*, 1929, pp. 85–92.

847. MEISSNER, W.: Messungen mit Hilfe von flüssigem Helium. III. Widerstand von Metallen (Measurements at Liquid Helium Temperatures. III. Resistance of Metals), *Z. ges. Kälte-Ind.*, v. 36, 1929, pp. 62–68.

848. OMA, K.: Sulphur in Electrolytic Iron and Its Removal, Inst. Phys. Chem. Research (Tokyo), *Bull.*, v. 8, 1929, pp. 126–130 (in Japanese). Abst.: Inst. Phys. Chem. Research (Tokyo), *Abstracts*, v. 2, 1929, pp. 19–20 (in English).

849. O'NEILL, H.: The Hardness of Vacuum-annealed Crystals of Iron, *J. Iron Steel Inst.*, v. 120, 1929, pp. 207–233.

850. OSAWA, A., and S. IWAIZUMI: X-ray Investigation of Iron and Nitrogen Alloys, *Sci. Rep.*, Sendai, ser. 1, v. 18, 1929, pp. 79–89.

851. OSAWA, A., and Y. OGAWA: X-ray Investigation of Iron and Zinc Alloys, *Sci. Rep.*, Sendai, ser. 1, v. 18, 1929, pp. 165–176.

852. PINCASS, H.: Das Eisencarbonyl (Iron Carbonyl), *Chemiker Z.*, v. 53, 1929, pp. 525–526.

853. RALSTON, O. C.: Iron Oxide Reduction Equilibria, *U. S. Bur. Mines Bull.* 296, 1929, pp. 157–159; 166–169; 172–182; 186–198.

854. ROBERTS, O. L., and W. P. DAVEY: An X-ray Study of the A_3 Point of Iron and Some Iron-nickel Alloys, *Metals & Alloys*, v. 1, 1929–1930, pp. 648–654.

855. ROGERS, B. A.: Change in Microstructure of Iron at A_3 Transformation Point, *Trans. Am. Inst. Min. Met. Eng.*, v. 84, 1929, pp. 370–380.

856. SAUERWALD, F., and K. A. POHLE: Über den Bruchvorgang in Eisen bei tiefen Temperaturen (Type of Fracture in Iron at Low Temperatures), *Z. f. Physik*, v. 56, 1929, pp. 576–578.

856*A*. SAUVEUR, A., and C. H. CHOU: The Gamma-alpha Transformation in Pure Iron, *Trans. Am. Inst. Min. Met. Eng.*, v. 84, 1929, pp. 350–369.

857. SCHMIDT, W.: Röntgenographische Untersuchungen über das System Eisen-Mangan (X-ray Investigation of the Iron-manganese System), *Archiv f. d. Eisenhüttenwesen*, v. 3, 1929–1930, pp. 293–300.

858. SEDERHOLM, P., and C. BENEDICKS: Studies of Overvoltage on Metals, *Trans. Am. Electrochem. Soc.*, v. 56, 1929, pp. 169–183.

859. SIEVERTS, A.: Die Aufnahme von Gasen durch Metalle (The Absorption of Gases by Metals), *Z. f. Metallkunde*, v. 21, 1929, pp. 37–44.

860. SIZOO, G. J.: Über das Magnetisierungsdiagramm von Eiseneinkristallen (Magnetization Diagram of Single Iron Crystals), *Z. f. Physik*, v. 56, 1929, pp. 649–670.

861. SIZOO, G. J., and C. ZWIKKER: Zur Kenntnis des Systems Nickel-Eisen (The System Nickel-iron), *Z. f. Metallkunde*, v. 21, 1929, pp. 125–126.

862. TAKEI, T., and T. MURAKAMI: On the Equilibrium Diagram of the Iron-molybdenum System, *Trans. Am. Soc. Steel Treat.*, v. 16, 1929, pp. 339–358.

863. TAMARU, K.: The Change in Specific Gravity of Cold-worked Iron and Steel by Tempering, Inst. Phys. Chem. Research (Tokyo), *Bull.*, v. 8, 1929, pp. 187–196 (in Japanese). Abst.: Inst. Phys. Chem. Research (Tokyo), *Abstracts*, v. 2, 1929, pp. 25–26 (in English).

864. TAMMANN, G.: Zur Theorie der Rekristallisation (Theory of Recrystallization), *Z. anorg. allgem. Chem.*, v. 185, 1929–1930, pp. 1–34.

865. THOMAS, T. P.: The Electrodeposition of Iron, *Metal Cleaning & Finishing*, v. 1, Sept. 1929, p. 464.

866. TRAILL, R. J., and W. R. McCLELLAND: Metallization of the Oxide of Iron in Ilmenite, *Can. Chem. Met.*, v. 13, 1929, pp. 265–268; 272.

867. UMINO, S.: On the Specific Heat of Pure Iron at High Temperatures, *Sci. Rep.*, Sendai, ser. 1, v. 18, 1929, pp. 91–107.

868. WARNER, J. C.: Organic Type Inhibitors in the Acid Corrosion of Iron, *Trans. Am. Electrochem. Soc.*, v. 55, 1929, pp. 287–296.

869. WATERHOUSE, G. B.: Sponge Iron by the Smith Process, *Iron Age*, v. 123, 1929, pp. 1143–1145.

870. WEVER, F., and A. MÜLLER: Über die Zweistoffsysteme Eisen-Bor und Eisen-Beryllium, mit einem Beitrag zur Kenntnis des Zweistoffsystems Eisen-Aluminium (The Binary Systems Iron-

boron and Iron-beryllium, with a Note on the Iron-aluminum System), *Mitt. K.-W. Inst. Eisenforschung*, v. 11, 1929, pp. 193–223.

871. YENSEN, T. D.: Pure Iron and Allotropic Transformations, *Trans. Am. Inst. Min. Met. Eng.*, v. 84, 1929, pp. 320–333. Gillett, H. W.: Discussion, pp. 334–339.

872. YENSEN, T. D.: Does Grain Size Influence the Magnetic Properties of Iron? *Metals & Alloys*, v. 1, 1929–1930, pp. 493–495.

1930

873. BAUMANN, K.: Some Considerations Affecting the Future Development of the Steam Cycle, *Proc. Inst. Mech. Eng.*, 1930, pp. 1305–1396.

874. CHARTKOFF, E. P., and W. P. SYKES: X-ray Notes on the Iron-molybdenum and Iron-tungsten Systems, *Trans. Am. Inst. Min. Met. Eng.*, v. 89, 1930, pp. 566–573.

875. CHITTUM, J. F.: The Electrochemical Behavior of Metals, *J. Phys. Chem.*, v. 34, 1930, pp. 2267–2285.

876. CIOFFI, P. P.: Hydrogenized Iron of High Magnetic Permeabilty, *Nature*, v. 126, 1930, pp. 200–201.

877. DEHLINGER, U.: Atomistische Grundlagen der Rekristallisation (Atomistic Basis of Recrystallization), *Z. f. Metallkunde*, v. 22, 1930, pp. 221–223.

878. EISENHUT, O., and E. KAUPP: Das System Eisen-Stickstoff (The Iron-nitrogen System), *Z. f. Elektrochemie*, v. 36, 1930, pp. 392–404.

879. EMMETT, P. H., S. B. HENDRICKS, and S. BRUNAUER: The Dissociation Pressure of Fe_4N, *J. Am. Chem. Soc.*, v. 52, 1930, pp. 1456–1464.

880. EUCKEN, A., and H. WERTH: Die spezifische Wärme einiger Metalle und Metallegierungen bei tiefen Temperaturen (The Specific Heat of Some Metals and Alloys at Low Temperatures), *Z. anorg. allgem. Chem.*, v. 188, 1930, pp. 152–172.

881. FORRER, R., and J. SCHNEIDER: Sur la production par les recuits des deux états du fer pur, stables à la température ordinaire (The Production by Annealing of Two Forms of Pure Iron, Stable at Ordinary Temperatures), *C. R. Acad. Sci.*, Paris, v. 190, 1930, pp. 1391–1393.

882. FRIAUF, J. B.: The Crystal Structure of an Iron Phosphide, *Trans. Am. Soc. Steel Treat.*, v. 17, 1930, pp. 499–508.

883. GERLACH, W.: "Die Bedeutung reinsten Eisens in kristallisierter Form für das Problem des Ferromagnetismus" (The Importance of Pure Iron in Crystalline Form for Problems in Ferromagnetism), Festschrift zum 70.Geb. von Heraeus, 1930, pp. 27–33.

884. GERLACH, W.: Über das magnetische Charakteristikum des Eisenkristalls (The Magnetic Characteristics of Iron Crystals), *Z. f. Physik*, v. 64, 1930, pp. 502–506.

885. GLASSTONE, S.: "The Electrochemistry of Solutions," Methuen & Co., Ltd., London, 1930, 476 pp.

886. GOUGH, H. J.: Fatigue of Single Crystals of Pure Metals, *First Communications New Int. Assoc. Test. Mat.*, Group A, 1930, pp. 133–138.

887. GUICHARD, CLAUSMANN, BILLON, and LANTHONY: La dureté du nickel, et du fer électrolytique (The Hardness of Electrolytic Nickel and Iron), VIme Congrès International Mines, Metallurgie et Géologie, Liége, 1930, *Section Métallurgie*, pp. 525–526.

888. HÄGG, G.: Röntgenuntersuchungen über die Nitride des Eisens (X-ray Studies of Iron Nitrides), *Z. phys. Chem.*, ser. B, v. 8, 1930, pp. 455–474.

889. HARRINGTON, R. H., and W. P. WOOD: Critical Ranges in Pure Iron-carbon Alloys, *Trans. Am. Soc. Steel Treat.*, v. 18, 1930, pp. 632–669; see also: v. 21, 1933, pp. 896–898.

890. HENDRICKS, S. B., and P. R. KOSTING: The Crystal Structure of Fe$_2$P, Fe$_2$N, Fe$_3$N and FeB, *Z. f. Kristallographie*, v. 74, 1930, pp. 511–533.

891. ISHIWARA, T.: On the Equilibrium Diagrams of the Aluminum-manganese, Copper-manganese, and Iron-manganese Systems, *Sci. Rep.*, Sendai, ser. 1, v. 19, 1930, pp. 499–519.

892. JENKINS, C. H. M., and M. L. V. GAYLER: The Optical Determination of High Metallurgical Temperatures—The Melting Point of Iron, *Proc. Royal Soc.* (London), ser. A, v. 129, 1930, pp. 91–114.

893. KOMMERS, J. B.: The Effect of Understressing on Cast Iron and Open-hearth Iron, *Proc. Am. Soc. Test. Mat.*, v. 30, part 2, 1930, pp. 368–381.

894. KURDJUMOW, G., and G. SACHS: Walz- und Rekristallisationstextur von Eisenblech (Rolling and Recrystallization Texture of Sheet Iron), *Mitt. deutsch. Materialprüfungsanstalten*, v. 13, 1930–1931, pp. 67–70. Also: *Z. f. Physik*, v. 62, 1930, pp. 592–599.

895. LEHRER, E.: Magnetische Untersuchungen über das System Eisen-Stickstoff (Magnetic Investigations of the Iron-nitrogen System), *Z. f. Elektrochemie*, v. 36, 1930, pp. 460–473.

896. MCAULAY, A. L., and G. L. WHITE: The Effect of Hydrogen Ion Concentration on the Electrode Potential of Iron, *J. Chem. Soc.*, 1930, pp. 194–199.

897. MEHL, R. F.: The Aging of Iron and Steel, *Iron and Steel of Canada*, v. 13, 1930, pp. 265–287.

898. MICHEL, A., and P. BÉNAZET: Influence du titane sur les points de transformation de l'acier (Influence of Titanium on the Transformation Points in Steel), *Rev. de Mét., Mém.*, v. 27, 1930, pp. 326–333.

899. MOORE, H. F., and T. VER: A Study of Slip Lines, Strain Lines, and Cracks in Metals under Repeated Stress, *Univ. of Illinois Bull.*, v. 27, No. 40, June 3, 1930 (*Bull.* 208, Engineering Experiment Station), 60 pp.

900. ÖHMAN, E.: Röntgenographische Untersuchungen über das System Eisen-Mangan (X-ray Investigation of the Iron-manganese System), *Z. phys. Chem.*, ser. B, v. 8, 1930, pp. 81–110.

901. PIKE, R. D., G. H. WEST, L. V. STECK, R. CUMMINGS, and B. P. LITTLE: Electrolytic Iron from Sulphide Ores, *Trans. Am. Inst. Min. Met. Eng.*, v. 90, 1930, pp. 311–343.

902. POMP, A.: Materialien bei hohen Temperaturen (Materials at High Temperatures), *First Communications New Int. Assoc. Test. Mat.*, Group A, Zurich, 1930, pp. 80–84.

903. REGNER, A.: The Magnetometric Determination of the Curie Points, *J. Iron Steel Inst.*, v. 122, 1930, pp. 343–364.

904. SAUVEUR, A.: Steel at Elevated Temperatures, *Trans. Am. Soc. Steel Treat.*, v. 17, 1930, pp. 410–448.

905. SIEGLERSCHMIDT, H.: Untersuchung des Einflusses der Umwandlung auf die Wärmeausdehnung von Stählen unter besonderer Berücksichtigung der Änderung der Ausdehnungszahl B (The Influence of the Transformation on the Thermal Expansion of Steels, Especially in Reference to the Change in Expansion Coefficient), *Mitt. deutsch. Materialprüfungsanstalten*, v. 13, 1930–1931, pp. 135–139.

906. SIMON, F., and R. BERGMANN: Thermisch erregte Quantensprünge in festen Körpern. IV. Messung der thermischen Ausdehnung im Gebiet der Anomalie (Thermally Excited Quantum Jumps in Solids. IV. Measurement of the Thermal Expansion in the Anomalous Region), *Z. physik. Chem.*, ser. B, v. 8, 1930, pp. 255–280.

907. SMITHELLS, C. J.: "Impurities in Metals," Chapman and Hall, Ltd., London, 2d ed. revised, 1930, 190 pp.

908. STIERSTADT, O.: Zur Frage der Widerstandsänderung von reinstem Elektrolyteisen in longitudinalen Magnetfeldern (The Change in Resistance of Purest Electrolytic Iron in Longitudinal Magnetic Fields), *Z. f. Physik*, v. 65, 1930, pp. 575–588.

909. TAMMANN, G.: Über die Rekristallisation (Recrystallization), *Z. f. Metallkunde*, v. 22, 1930, pp. 224–226.

910. TAMMANN, G., and W. CRONE: Zur Rekristallisation der Metalle (Recrystallization of Metals), *Z. anorg. allgem. Chem.*, v. 187, 1930, pp. 289–312.

911. THOMAS, C. T., and W. BLUM: The Production of Electrolytic Iron Printing Plates, *Trans. Am. Electrochem. Soc.*, v. 57, 1930, pp. 59–71.

911A. WENSEL, H. T., and W. F. ROESER: The Freezing Point of Nickel as a Fixed Point on the International Temperature Scale, *National Bur. Stds. J. Res.*, v. 5, 1930, pp. 1309–1318.

912. WEVER, F., and W. JELLINGHAUS: Zur Kenntnis des Zweistoffsystems Eisen-Vanadium (The Binary System Iron-vanadium), *Mitt. K.-W. Inst. Eisenforschung*, v. 12, 1930, pp. 317–322.

913. ZIEGLER, N. A.: Production and Some Properties of Large Iron Crystals, *Trans. Am. Inst. Min. Met. Eng.*, v. 90, 1930, pp. 209–223.

1931

914. ABEGG, R.: "Handbuch der anorganischen Chemie" (Handbook of Inorganic Chemistry), S. Hirzel, Leipzig, 1931, v. 4.

915. ALTERTHUM, H.: Die Entwicklung auf dem Gebiete der temperaturbedingten Kristallstrukturänderungen von homogenen festen Metallen (Developments in the Field of Temperature-dependent Changes in Crystal Structure of Homogeneous Solid Metals), *Physik. Z.*, v. 32, 1931, pp. 305–326.

916. BANNISTER, C. O., and W. D. JONES: The Diffusion of Tin into Iron with Special Reference to the Formation of Columnar Crystals, *J. Iron Steel Inst.*, v. 124, 1931, pp. 71–93.

917. BATES, A. A.: Aging in Low-carbon Steels, *Trans. Am. Soc. Steel Treat.*, v. 19, 1931–1932, pp. 449–471.

918. BENEDICKS, C., and H. LÖFQUIST: "Non-metallic Inclusions in Iron and Steel," John Wiley & Sons, Inc., New York, 1931, 311 pp.

919. BRUNAUER, S., M. E. JEFFERSON, P. H. EMMETT, and S. B. HENDRICKS: Equilibria in the Iron-nitrogen System, *J. Am. Chem. Soc.*, v. 53, 1931, pp. 1778–1786.

920. DIERGARTEN, H., and W. EILENDER: Stickstoffseigerung im Stahl (Segregation of Nitrogen in Steel), *Stahl u. Eisen*, v. 51, 1931, pp. 231–232.

921. DIXON, J. R., and W. STEINER: Über die Reaktion von aktivem Stickstoff mit Wasserstoffatomen an metallischen Oberflächen (The Reaction of Active Nitrogen with Atomic Hydrogen on Metallic Surfaces), *Z. phys. Chem.*, ser. B, v. 14, 1931, pp. 397–406.

922. EDWARDS, C. A., and A. PREECE: A Study of the Constitution of the Iron-tin Alloys, *J. Iron Steel Inst.*, v. 124, 1931, pp. 41–66.

923. EHN, E. W.: Seasoning of Steel, *Metal Progress*, v. 20, Sept. 1931, pp. 59–64; 108.

924. ENDO, H., and S. KANAZAWA: Single Potential of Iron and Steel Electrodes, *Sci. Rep.*, Sendai, ser. 1, v. 20, 1931, pp. 124–139.

925. FELL, E. W.: Untersuchungen über den Einfluss von Sauerstoff und Schwefel auf die Schmiedbarkeit, Rotbrüchigkeit und andere Eigenschaften des reinen Eisens (Study of the Influence of Oxygen and Sulphur on the Forgeability, Red Shortness, and Other Properties of Pure Iron), *Archiv f. d. Eisenhüttenwesen*, v. 4, 1931, pp. 393–400.

926. FRANCE, R. D.: Endurance Testing of Steel, *Proc. Am. Soc. Test. Mat.*, v. 31, part 2, 1931, pp. 176–199.

927. GROESBECK, E. C., and L. J. WALDRON: Oxygen as a Factor in Submerged Corrosion, *Proc. Am. Soc. Test. Mat.*, v. 31, part 2, 1931, pp. 279–293.

928. HENSEL, F. R., and E. I. Larsen: Dissolved Nitrogen Embrittles Weld Metal, *Metal Progress*, v. 20, Sept. 1931, pp. 44–47.

929. LOGAN, K. H., and V. A. GRODSKY: Soil Corrosion Studies, 1930, *National Bur. Stds. J. Res.*, v. 7, 1931, pp. 1–35; 585–605.

930. MATHEWSON, C. H., E. SPIRE, and W. E. MILLIGAN: Evolution of the Iron-oxygen Constitution Diagram, *Trans. Am. Soc. Steel Treat.*, v. 19, 1931–1932, pp. 66–88.

931. NORTHRUP, E. F.: Tonnage Melting by Coreless Induction, *Iron Age*, v. 127, 1931, pp. 228–233.

932. NORTHRUP, E. F.: Power Problems in High-frequency Melting, *Iron Age*, v. 127, 1931, pp. 318–322.

933. NORTHRUP, E. F.: Typical Installations of Coreless Induction Furnaces, *Iron Age*, v. 127, 1931, pp. 395–399; 447–448.

934. PALMAER, W.: The Corrosion of Metals. Theory and Experiments. Part II. Special Researches concerning the Dissolving of Metals, *Ingeniörs Vetenskaps Akademien, Handlingar*, No. 108, 1931, 198 pp. Reviewed: *J. Inst. Metals*, v. 47, 1931, p. 687; *Chem. Absts.*, v. 26, 1932, p. 3220.

935. PFANHAUSER, W.: Eisen (Iron), in V. Engelhardt's "Handbuch der technischen Elektrochemie," Akademische Verlagsgesellschaft m. b. H., Leipzig, 1931, v. 1, part 1: Die technische Elektrolyse wässeriger Lösungen, pp. 217–275.

936. PORTEVIN, A., and A. SANFOURCHE: Sur l'attaque des métaux usuels par les solutions phosphoriques (The Attack of Common Metals by Phosphoric Acid Solutions), *C. R. Acad. Sci.*, Paris, v. 192, 1931, pp. 1563–1565.

937. ROGERS, B. A.: A Furnace for Metallographic Examination of Specimens at High Temperatures, *Metals & Alloys*, v. 2, 1931, pp. 9–12.

938. SATÔ, S.: On the Thermal Measurement of the Latent Energy in Cold Worked Metals and Alloys, *Sci. Rep.*, Sendai, ser. 1, v. 20, 1931, pp. 140–177.

939. SAUERWALD, F., and W. SCHOLZ: Ein Beitrag zum Zeitgesetz der Entfestigung verformter Metalle (Rate of Loss of Strength in Worked Metals), *Z. f. Physik*, v. 73, 1931–1932, pp. 511–525.

940. SCHLECHT, L., W. SCHUBARDT, and F. DUFTSCHMID: Über die Verfestigung von pulverförmigem Carbonyleisen durch Wärme- und Druckbehandlung (Compacting Powdered Carbonyl Iron by Heat Treatment and Pressure), *Z. f. Elektrochemie*, v. 37, 1931, pp. 485–492.

941. SCOTT, F. W.: Effect of Nitrogen on Steel. A Practical Consideration as Applied to Commercial Open-hearth Steel, *J. Ind. Eng. Chem.*, v. 23, 1931, pp. 1036–1051.

942. SIEVERTS, A.: Die Absorption von Stickstoff durch Eisen (The Absorption of Nitrogen by Iron), *Z. phys. Chem.*, ser. A, v. 155, 1931, pp. 299–313.

943. SODERBERG, G.: Rust and Rust Prevention, *Monthly Rev. Am. Electroplaters Soc.*, v. 18, No. 5, 1931, pp. 15–28.

944. STANSFIELD, A.: The Corrosion of Metals, *Eng. J.*, v. 14, 1931, pp. 444–446.

945. STIERSTADT, O.: Die elektrische Widerstandsänderung von reinstem Elektrolyteisen in transversalen Magnetfeldern (The Change in Electric Resistance of Pure Electrolytic Iron in Transverse Magnetic Fields), *Z. f. Physik*, v. 67, 1931, pp. 725–742.

946. SWANGER, W. H., and F. R. CALDWELL: Special Refractories for Use at High Temperatures, *National Bur. Stds. J. Res.*, v. 6, 1931, pp. 1131–1143.

947. SYKES, W. P.: Composition Limits of the Alpha-gamma Loop in the Iron-tungsten System, *Trans. Am. Inst. Min. Met. Eng.*, v. 95, 1931, pp. 307–311.

948. TAMMANN, G., and F. NEUBERT: Der Einfluss von Fremdmetallen auf die Auflösungsgeschwindigkeit unedler Metalle (Influence of Foreign Metals on the Rate of Solution of Base Metals), *Z. anorg. allgem. Chem.*, v. 201, 1931, pp. 225–244.

949. THOMAS, T. P.: Repairing Worn Parts by Electrodeposition, *Trans. Am. Soc. Mech. Eng.*, v. 53, 1931, MSP 53-4, pp. 29–30. Also: *Machinery*, New York, v. 37, 1930–1931, pp. 134–135.

950. TRAVERS, A., and J. AUBERT: Étude du couple Fe, FeS. Passivation de FeS (Study of the Couple Fe, FeS. Passivation of FeS), *Chimie et Industrie*, v. 26, 1931, p. 1040. Abst.: *Metals & Alloys*, v. 3, 1932, p. MA202.

951. WASMUHT, R.: Die Ausscheidungshärtung des Eisens durch Titan (Precipitation Hardening of Iron by Titanium), *Archiv f. d. Eisenhüttenwesen*, v. 5, 1931–1932, pp. 45–56. Also: *Kruppsche Monatshefte*, v. 12, 1931, pp. 159–177.

952. WINTER, E.: Der katalytische Ammoniakzerfall an Eisen (Catalytic Decomposition of Ammonia over Iron), *Z. phys. Chem.*, ser. B, v. 13, 1931, pp. 401–424.

953. YAP, CHU-PHAY: A Thermodynamic Study of the Phasial Equilibria in the System Iron-carbon, *Am. Inst. Min. Met. Eng.*, *Tech. Pub.* 381, 1931, 26 pp.

954. YENSEN, T. D., and N. A. ZIEGLER: Magnetic Properties versus Allotropic Transformations of Iron Alloys, *Trans. Am. Inst. Min. Met. Eng.*, v. 95, 1931, pp. 313–317.

1932

955. AUSTIN, J. B.: Heat Capacity of Iron, *J. Ind. Eng. Chem.*, v. 24, 1932, pp. 1225–1235.

956. AUSTIN, J. B.: Entropy, Heat Content, and Free Energy of Iron, *J. Ind. Eng. Chem.*, v. 24, 1932, pp. 1388–1391.

957. BAIN, E. C.: Factors Affecting the Inherent Hardenability of Steel, *Trans. Am. Soc. Steel Treat.*, v. 20, 1932, pp. 385–428.

958. BENTON, A. F., and T. A. WHITE: The Sorption of Gases by Iron, *J. Am. Chem. Soc.*, v. 54, 1932, pp. 1820–1830.

959. BITTER, F.: Experiments on the Nature of Ferromagnetism, *Phys. Rev.*, v. 41, 1932, pp. 507–515.

960. BODFORSS, S.: Zur Elektrochemie des Eisens (Electrochemistry of Iron), *Z. phys. Chem.*, ser. A, v. 160, 1932, pp. 141–157.

961. BORGMANN, C. W.: Corrosion of Iron, *Bell Lab. Record*, v. 10, 1932, pp. 230–233.

962. BRADLEY, A. J., and A. H. JAY: The Lattice Spacing of Iron-aluminum Alloys, *J. Iron Steel Inst.*, v. 125, 1932, pp. 339–357.

963. BULL-SIMONSEN, I.: Betriebsmässige Erzeugung von Eisenschwamm nach dem Norsk-Staal-Verfahren (Large-scale Manufacture of Sponge Iron by the Norsk-Staal Process), *Stahl u. Eisen*, v. 52, 1932, pp. 457–461.

964. CIOFFI, P. P.: Hydrogenized Iron, *Bell Lab. Record*, v. 10, 1932, pp. 159–163. Also: *Phys. Rev.*, v. 39, 1932, pp. 363–367.

965. DUFTSCHMID, F., L. SCHLECHT, and W. SCHUBARDT: Die technische Verarbeitung von pulverförmigem Carbonyleisen nach dem Sinterverfahren (The Technical Treatment of Carbonyl Iron Powder by the Sintering Process), *Stahl u. Eisen*, v. 52, 1932, pp. 845–849.

966. FRIEND, J. N.: The Relative Corrodibilities of Ferrous and Nonferrous Metals and Alloys, Part III, *J. Inst. Metals*, v. 48, 1932, pp. 109–116.

967. GOENS, E., and E. SCHMID: Über die elastische Anisotropie des Eisens (Elastic Anisotropy of Iron), *Mitt. deutsch. Materialprüfungsanstalten*, No. 19, 1932, pp. 84–87.

968. GRAY, H. H., and M. B. THOMPSON: The Action of Molecular Nitrogen on Highly Purified Iron, *J. Phys. Chem.*, v. 36, 1932, pp. 889–908.

969. GREGG, J. L.: "The Alloys of Iron and Molybdenum," McGraw-Hill Book Company Inc., New York, 1932, 507 pp.

970. HANEMANN, H., A. SCHRADER, and W. TANGERDING: Der Aederungsbestandteil im Ferrit (The Veining Constituent in Ferrite), *Archiv f. d. Eisenhüttenwesen*, v. 6, 1932–1933, pp. 567–570.

971. HILL, A. G.: On Magnetic Effects in Iron Crystals, *Phil. Mag.*, v. 14, 1932, pp. 599–604.

972. HOMER, C. E.: The Influence of Non-metallic Inclusions on the Corrosion of Steels, *Iron Steel Inst., Carn. Schol. Mem.*, v. 21, 1932, pp. 35–37.

973. JACQUÉ, L.: Sur l'altération des aciers par l'hydrogène (Alteration of Steels by Hydrogen), *C. R. Acad. Sci.*, Paris, v. 195, 1932, pp. 878–880.

974. KUNZE, O.: Die Erzeugung von Eisenschwamm nach dem Norsk-Staal-Verfahren (Production of Sponge Iron by the Norsk-Staal Process), *Elektrowärme*, v. 2, 1932, pp. 197–200. Abst.: *Metals & Alloys*, v. 4, 1933, p. MA401.

975. LIEBREICH, E.: Das Eisen als Wasserstoffelektrode (Iron as a Hydrogen Electrode), *Z. phys. Chem.*, ser. A, v. 161, 1932, pp. 97–112.

976. MESSKIN, W. S., and J. M. MARGOLIN: Einfluss von Wasserstoff auf Transformatorenstahl (Influence of Hydrogen on Transformer Steel), *Archiv f. d. Eisenhüttenwesen*, v. 6, 1932–1933, pp. 399–405.

977. MITTASCH, A., and E. KEUNECKE: Über die Aktivierung von Eisen durch Aluminiumoxyd bei der Ammoniak-Katalyse (The Activation of Iron by Means of Aluminum Oxide, for the Synthesis of Ammonia), *Z. f. Elektrochemie*, v. 38, 1932, pp. 666–669.

978. MÜLLER, W. J., and W. MACHU: Zur Theorie der Passivitätserscheinungen, XV (Theory of Passivity, XV), *Monatsh. f. Chemie*, v. 60, 1932, pp. 359–385.

979. POULTER, T. C., and L. UFFELMAN: The Penetration of Hydrogen through Steel at Four Thousand Atmospheres, *Physics*, v. 3, 1932, pp. 147–148.

980. Report on Proposed American Standard Definitions of Electrical Terms, Published by the Am. Inst. Elec. Eng., New York, 1932, 205 pp.

981. RESCHKA, J.: Beitrag zur Frage des Sauerstoffs im Eisen (Oxygen in Iron), *Mitt. a. d. Forschungs-Institut der Vereinigte Stahlwerke, Dortmund*, v. 3, No. 1, 1932, pp. 1–18.

982. SELJESATER, K. S., and B. A. ROGERS: Magnetic and Mechanical Hardness of Dispersion-hardened Iron Alloys, *Trans. Am. Soc. Steel Treat.*, v. 19, 1932, pp. 553–572.

983. STIERSTADT, O.: Die Änderungen der elektrischen Leitfähigkeit ferromagnetischer Stoffe in Magnetfeldern (The Change of Conductivity of Ferromagnetic Materials in Magnetic Fields), *Z. tech. Phys.*, v. 13, 1932, pp. 65–71; 105–111; 161–165.

984. TRAVERS, A., and J. AUBERT: Sur la passivité du fer électrolytique en milieu alcalin (Passivity of Electrolytic Iron in Alkaline Solutions), *C. R. Acad. Sci.*, Paris, v. 194, 1932, pp. 2308–2309.

985. TRAVERS, A., and J. AUBERT: Variations du potentiel du fer électrolytique avec le pH du milieu (Variations of Potential of Electrolytic Iron with pH of the Medium), *C. R. Acad. Sci.*, Paris, v. 195, 1932, pp. 138–139.

986. VAN ARKEL, A. E.: La préparation de quelques métaux rares par dissociation thermique (The Preparation of Several Rare Metals by Thermal Dissociation), *Rev. univ. Mines*, ser. 8, v. 8, 1932, pp. 37–41.

987. WALTERS, F. M., JR., and associates: Alloys of Iron, Manganese, and Carbon. Parts I to IV and IX, *Trans. Am. Soc. Steel Treat.*, v. 19, 1932, pp. 577–623; v. 21, 1933, pp. 1002–1013.

988. YAP, CHU-PHAY: The Free Energy of Transition of Iron $(\alpha \rightleftharpoons \gamma)$, *Trans. Faraday Soc.*, v. 28, 1932, pp. 781–788.

989. YENSEN, T. D.: Effect of Impurities on Ferromagnetism, *Phys. Rev.*, v. 39, 1932, pp. 358–363.

1933

990. AMMERMANN, E., and H. KORNFELD: Die Aederung des Ferrits (The Veining of Ferrite), *Archiv f. d. Eisenhüttenwesen*, v. 7, 1933–1934, pp. 567–570.

991. ANON.: Develops New Pure Iron Suitable for Many Uses, *Steel*, v. 92, March 27, 1933, p. 23.

992. ASTON, F. W.: "Mass Spectra and Isotopes," Edwin Arnold and Co., London, 1933, 248 pp.

993. BITTER, F.: Magnetism and the Structure of Metals, *Mech. Eng.*, v. 55, 1933, p. 287.

994. DEHAAS, W. J., and R. A. HADFIELD: On the Effect of the Temperature of Liquid Hydrogen ($-252.8°$C.) on the Tensile Properties of Forty-one Specimens of Metals Comprising (a) Pure Iron 99.85%; (b) Four Carbon Steels; (c) Thirty Alloy Steels; (d) Copper and Nickel; (e) Four Non-ferrous Alloys, *Phil. Trans. Royal Soc.* (London), ser. A, v. 232, 1933–1934, pp. 297–332.

995. ESSER, H., and H. CORNELIUS: Einfluss von Wasserstoff auf die A_3- und A_1-Umwandlungen des Eisens (Influence of Hydrogen on the A_3 and A_1 Transformations in Iron), *Stahl u. Eisen*, v. 53, 1933,

pp. 885–886. Also: *Trans. Am. Soc. Steel Treat.*, v. 21, 1933, pp. 733–740.

996. ESSER, H., and H. CORNELIUS: Gefügeuntersuchung bei Temperaturen bis 1100° (Metal Microscopy at High Temperatures), *Stahl u. Eisen*, v. 53, 1933, pp. 532–535. Also: *Metals & Alloys*, v. 4, 1933, pp. 119–122.

997. ESSER, H., and G. MÜLLER: Die Gitterkonstanten von reinem Eisen und Eisen-Kohlenstoff-Legierungen bei Temperaturen bis 1100° (The Lattice Constants of Pure Iron and Iron-carbon Alloys at Temperatures up to 1100°), *Archiv f. d. Eisenhüttenwesen*, v. 7, 1933–1934, pp. 265–268.

998. FAHRENHORST, W., and E. SCHMID: Über die plastische Dehnung von Alpha-Eisenkristallen (The Plastic Elongation of Crystals of Alpha Iron), *Mitt. deutsch. Materialprüfungsanstalten*, v. 21, 1933, pp. 52–57.

999. GOUGH, H. J.: Crystalline Structure in Relation to Failure of Metals, Especially by Fatigue, *Proc. Am. Soc. Test. Mat.*, v. 33, part 2, 1933, pp. 3–105.

1000. GREINER, E. S., J. S. MARSH, and B. STOUGHTON: "The Alloys of Iron and Silicon," McGraw-Hill Book Company Inc., New York, 1933, 457 pp.

1001. GREGG, J. L., and B. N. DANILOFF: Constitution of Iron-copper Alloys, "National Metals Handbook," Am. Soc. Steel Treat., Cleveland, 1933, pp. 324–328.

1002. HAYAKAWA, K.: Studies on the Transformation of Metals by Secondary Electron Emission, *Sci. Rep.*, Sendai, ser. 1, v. 22, 1933, pp. 934–958.

1003. HEINDLHOFER, K., and B. M. LARSEN: Rates of Scale Formation on Iron and a Few of Its Alloys, *Trans. Am. Soc. Steel Treat.*, v. 21, 1933, pp. 865–895.

1004. HENSEL, F. R., and T. F. HENGSTENBERG: Some Observations on the Effects of Inclusions on the Tensile and Dynamic Properties of Certain Ferrous Materials, Am. Inst. Min. Met. Eng., *Preprint*, 1933, 27 pp.

1005. HENSEL, F. R., and E. I. LARSEN: A Note on the A_3 Point of Highly Purified Iron, *Metals & Alloys*, v. 4, 1933, pp. 37–38.

1006. HOMERBERG, V. O.: Nitriding, "National Metals Handbook," Am. Soc. Steel Treat., Cleveland, 1933, pp. 938–957.

1007. JETTE, E. R., and E. S. Greiner: An X-ray Study of Iron-silicon Alloys containing 0 to 15 Per Cent Silicon, *Trans. Am. Inst. Min. Met. Eng.*, v. 105, 1933, pp. 259–275.

1008. KANNULUIK, W. G.: The Thermal and Electrical Conductivities of Several Metals Between −183° and 100°C., *Proc. Royal Soc.* (London), ser. A, v. 141, 1933, pp. 159–168.

1009. KAYA, S.: Über die Remanenz von Eiseneinkristallen (Remanence of Single Iron Crystals), *Z. f. Physik*, v. 11, 1933, pp. 705–716.

1010. KENYON, R. L., and R. F. MEHL: Effect of Plastic Deformation on the Physical and Mechanical Properties of Pure Iron, "National

Metals Handbook," Am. Soc. Steel Treat., Cleveland, 1933, pp. 399–405.

1011. KÖRBER, F., and H. PLOUM: Über die Aufnahme des Wasserstoffs durch Eisen (The Occlusion of Hydrogen by Iron), *Z. f. Elektrochemie*, v. 39, 1933, pp. 252–255.

1012. KRIVOBOK, V. N., and C. WELLS: Constitution of Iron-manganese Alloys, "National Metals Handbook," Am. Soc. Steel Treat., Cleveland, 1933, pp. 329–333.

1013. KRIVOBOK, V. N., and C. Wells: Alloys of Iron, Manganese and Carbon; Part V, *Trans. Am. Soc. Steel Treat.*, v. 21, 1933, pp. 807–820.

1014. LEWKONJA, G., and W. BAUKLOH: Über die Wasserstoffdurchlässigkeit von Armco-Eisen und Eisen mit verschiedenen Kohlenstoffgehalten bei Temperaturen von 700 bis 1000°C. (The Permeability to Hydrogen of Armco Iron and Iron with Different Carbon Contents at Temperatures from 700 to 1000°C.), *Z. f. Metallkunde*, v. 25, 1933, pp. 309–310.

1015. LOCHTE, H. L., and R. E. Paul: The Electrochemical Behavior of Iron in Corrosion Cells, *Trans. Electrochem. Soc.*, v. 64, 1933, pp. 155–188.

1016. LOGAN, K. H.: The Protection of Pipes against Soil Action, *Trans. Electrochem. Soc.*, v. 64, 1933, pp. 113–124.

1017. LUCKEMEYER-HASSE, L., and H. SCHENCK: Löslichkeit von Wasserstoff in einigen Metallen und Legierungen (The Solubility of Hydrogen in Some Metals and Alloys), *Tech. Mitt. Krupp*, v. 1, 1933, pp. 121–126.

1018. MATHEWSON, C. H.: Plastic Deformation of Pure Iron, "National Metals Handbook," Am. Soc. Steel Treat., Cleveland, 1933, pp. 392–397.

1019. MERICA, P. D.: Constitution of Iron-nickel Alloys, "National Metals Handbook," Am. Soc. Steel Treat., Cleveland, 1933, pp. 339–342.

1020. OWEN, E. A., and E. L. Yates: Precision Measurements of Crystal Parameters, *Phil. Mag.*, v. 15, 1933, pp. 472–488.

1021. ÔSAWA, A.: On the Equilibrium Diagram of Iron-aluminum System, *Sci. Rep.*, Sendai, ser. 1, v. 22, 1933, pp. 803–823.

1022. PASSANO, R. F., and F. R. NAGLEY: Consistent Data Showing the Influence of Water Velocity and Time on the Corrosion of Iron, *Proc. Am. Soc. Test. Mat.*, v. 33, part 2, 1933, pp. 387–399.

1023. SAKLATWALLA, B. D., and J. STRAUSS: Constitution of Iron-vanadium Alloys, "National Metals Handbook," Am. Soc. Steel Treat., Cleveland, 1933, pp. 362–364.

1024. SAUERWALD, F., and W. GLOBIG: Über die Geschwindigkeit der Entfestigung verformter Metalle durch Erholung und Rekristallisation (Rate of Softening of Deformed Metals by Relaxation and Recrystallization), *Z. f. Metallkunde*, v. 25, 1933, pp. 33–38.

1025. SAUERWALD, F., and H. G. SOSSINKA: Über Sprödigkeit, Plastizität und die Gleitelemente des Alpha-Eisens (Brittleness, Plasticity, and Twinning in Alpha Iron), *Z. f. Physik*, v. 82, 1933, pp. 634–643.

1026. Sauveur, A., and J. L. Burns: A Method for Studying Strain Hardening Susceptibility and Aging after Cold Work Deformation, *Metals & Alloys*, v. 4, 1933, p. 6.

1027. Schikorr, G.: Über die Theorie der Korrosion des Eisens (Theory of the Corrosion of Iron), *Mitt. deutsch. Materialprüfungsanstalten*, No. 22, 1933, pp. 9–16.

1028. Schmidt, W.: Über thermische Ausdehnungsmessungen an Eisen mittels Röntgenstrahlen (Measurements of the Thermal Dilatation of Iron by Means of X-rays), in "Ergebnisse der technischen Röntgenkunde. III. Wechselwirkung zwischen Röntgenstrahlen und Materie in Theorie und Praxis," Akademische Verlagsgesellschaft m.b.H., Leipzig, 1933, pp. 194–201.

1029. Speller, F. N.: Discussion of Paper by W. H. J. Vernon, on The Rôle of The Corrosion Product in the Atmospheric Corrosion of Iron, *Trans. Electrochem. Soc.*, v. 64, 1933, p. 41.

1030. Tammann, G., and G. Bandel: Die Änderung der Thermokraft bei der Erholung der Metalle von der Kaltbearbeitung (The Change in Thermoelectric Power of Metals on Recovery from Cold Working), *Ann. d. Physik*, ser. 5, v. 16, 1933, pp. 120–128.

1031. Tammann, G., and G. Moritz: Über die Erholung von der Kaltbearbeitung beim Eisen und Nickel (The Recovery of Iron and Nickel from Cold Working), *Ann. d. Physik*, ser. 5, v. 16, 1933, pp. 667–679.

1032. Tiemann, H. P.: "Iron and Steel," McGraw-Hill Book Company Inc., New York, 3d ed., 1933, 590 pp.

1033. Toporescu, E.: Sur la corrosion du fer (The Corrosion of Iron), *C. R. Acad. Sci.*, Paris, v. 197, 1933, pp. 1040–1041. Abst.: *Chem. Absts.*, v. 28, 1934, p. 1647.

1034. Tronstad, L., and J. Sejersted: The Effect of Sulphur and Phosphorus on the Corrosion of Iron, *J. Iron Steel Inst.*, v. 127, 1933, pp. 425–436.

1035. Vernon, W. H. J.: The Rôle of the Corrosion Product in the Atmospheric Corrosion of Iron, *Trans. Electrochem. Soc.*, v. 64, 1933, pp. 31–41.

1036. Watts, O. P.: The Electrochemical Theory of Corrosion, *Trans. Electrochem. Soc.*, v. 64, 1933, pp. 125–150.

1037. Wever, F., and B. Pfarr: Über die Ausbildung von Gitterstörungen bei der Kaltverformung und ihre Rückbildung bei der Kristallerholung und Rekristallisation (Disturbances in the Lattice as a Result of Cold Working and the Subsequent Recovery and Recrystallization), *Mitt. K.-W. Inst. Eisenforschung*, v. 15, 1933, pp. 137–145.

1038. Wever, F., and B. Pfarr: Über die Gitterparameteränderung des α-Eisens bei der Wasserstoffbeladung (The Change in Lattice Parameter of Alpha Iron as a Result of Absorption of Hydrogen), *Mitt. K.-W. Inst. Eisenforschung*, v. 15, 1933, pp. 147–148.

1039. Winter, F.: Die Reindarstellung von Eisen und Nickel (Production of Pure Iron and Nickel), *Metallbörse*, v. 23, 1933, pp. 957–958.

1040. ZIEGLER, N. A.: Pure Iron, *Metal Progress*, v. 24, Oct. 1933, pp. 26–29; 68.

1934

1041. ABRAM, H. H.: The Value of Young's Modulus for Steel, *J. Iron Steel Inst.*, v. 129, 1934, pp. 325–330.

1042. AKULOV, N., and S. Raewsky: Über den Mechanismus der plastischen Deformation der Eiseneinkristalle (The Mechanism of Plastic Deformation in Single Crystals of Iron), *Ann. d. Physik*, ser. 5, v. 20, 1934, pp. 113–117.

1043. ANON.: Huckleberry Swamp Corrodes Tower Footing, *Elec. World*, v. 102, 1933, p. 735. Abst.: *Metals & Alloys*, v. 5, 1934, p. MA294.

1044. ANON.: The National Physical Laboratory, *Engineering*, v. 138, 1934, p. 150.

1045. AUSTIN, C. R., and J. R. GIER: Comparative Studies on Creep of Metals Using a Modified Rohn Test, *Trans. Am. Inst. Min. Met. Eng.*, v. 111, 1934, pp. 53–74.

1046. AUSTIN, J. B., and R. H. H. PIERCE, JR.: The Linear Thermal Expansion and Alpha-gamma Transformation Temperature (A_3 Point) of Pure Iron, *Trans. Am. Soc. Metals*, v. 22, 1934, pp. 447–467.

1047. BAXTER, G. P., M. CURIE, O. HÖNIGSCHMID, P. LEBEAU, and R. J. MEYER: Fourth Report of the Committee on Atomic Weights of the International Union of Chemistry, *J. Am. Chem. Soc.*, v. 56, 1934, pp. 753–763.

1048. BURNS, J. L.: Classification of Alpha Iron-nitrogen and Alpha Iron-carbon as Age-hardening Alloys, *Trans. Am. Inst. Min. Met. Eng.*, v. 113, 1934, pp. 239–261.

1049. CIOFFI, P. P.: New High Permeabilities in Hydrogen-treated Iron, *Phys. Rev.*, v. 45, 1934, p. 742.

1050. DEAN, R. S., *et al.*: Progress Reports—Metallurgical Division, United States Bureau of Mines, *Report of Investigations* No. 3229, May 1934, 70 pp.

1050A. DESCH, C. H.: The Work of the Alloys of Iron Research Committee, *Proc. Inst. Mech. Eng.*, v. 127, 1934, pp. 277–298.

1051. EISENKOLB, F.: Über die Bewitterungsversuche mit Feinblechen aus weichem Stahl (Resistance of Mild-steel Sheets to Atmospheric Agencies), *Korrosion u. Metallschutz*, v. 10, 1934, pp. 161–166.

1052. ELLIS, W. C., and SCHUMACHER, E. E.: Magnetic Materials, *Metals & Alloys*, v. 5, 1934, pp. 269–276.

1053. ESSER, H., and W. BUNGHARDT: Einfluss des Untersuchungsverfahrens auf den gemessenen Wärmeinhalt des Eisens (Influence of the Method of Determination on the Measured Heat Content of Iron), *Archiv f. d. Eisenhüttenwesen*, v. 8, 1934, pp. 37–38.

1054. GREGG, J. L.: "The Alloys of Iron and Tungsten," McGraw-Hill Book Company, Inc., New York, 1934, 511 pp.

1055. GREGG, J. L., and B. N. DANILOFF: "The Alloys of Iron and Copper," McGraw-Hill Book Company, Inc., New York, 1934, 454 pp.

1056. HEINDLHOFER, K.: The "Plasticity" of Iron at Low Temperatures, Am. Inst. Min. Met. Eng., *Tech. Pub.* No. 581, *Metals Technology*, October 1934, 7 pp.

1057. JETTE, E. R., W. L. BRUNER, and F. FOOTE: An X-ray Study of Gold-iron Alloys, *Trans. Am. Inst. Min. Met. Eng.*, v. 111, 1934, pp. 354–360.

1058. KARSCHULIN, M.: Über periodische Potentialschwankungen des Eisens in Chrom-Schwefelsäure-Lösungen (Periodic Fluctuations in the Potential of Iron in Solutions of Mixed Chromic and Sulphuric Acids), *Z. f. Elektrochemie*, v. 40, 1934, pp. 174–180; 559–564.

1059. KIMURA, R., and K. OHNO: On the Elastic Constants of Single Crystals of Iron, *Sci. Rep.*, Sendai, ser. 1, v. 23, 1934, pp. 359–364.

1060. KROLL, W.: Über das sublimierte Eisen (Sublimed Iron), *Z. f. Elektrochemie*, v. 40, 1934, pp. 303–306.

1061. LOGAN, K. H., and R. H. TAYLOR: Soil Corrosion Studies, 1932. *National Bur. Stds. J. Res.*, v. 12, 1934, pp. 119–144.

1062. LOPUCHIN, E.: Magnetische Eigenschaften von Stahl und Eisen bei Dehnung (Magnetic Properties of Iron and Steel during Stretching), *Phys. Z. d. Sowjetunion*, v. 5, 1934, pp. 57–74.

1063. MEHL, R. F., C. S. BARRETT, and H. S. JERABEK: Studies upon the Widmanstätten Structure, VI.—Iron-rich Alloys of Iron and Nitrogen and of Iron and Phosphorus, *Trans. Am. Inst. Min. Met. Eng.*, v. 113, 1934, pp. 211–229.

1064. MEHL, R. F., and D. W. SMITH: Studies upon the Widmanstätten Structure, V.—The Gamma-alpha Transformation in Pure Iron, *Trans. Am. Inst. Min. Met. Eng.*, v. 113, 1934, pp. 203–210.

1065. NORTHCOTT, L.: Veining of Ferrite, *Metallurgist*, v. 10, 1934, pp. 163–165.

1066. NORTON, J. T.: Solubility of Copper in Iron, and Lattice Changes during Aging, Am. Inst. Min. Met. Eng., *Tech. Pub.* No. 586, *Metals Technology*, December 1934, 9 pp.

1067. POBOŘIL, F.: Étude thermodynamique de la forme du silicium dissous dans le fer liquide (Thermodynamic Study of the State of Silicon Dissolved in Liquid Iron), *Chimie et Industrie*, Special Number, April 1934, pp. 480–484.

1068. PORTEVIN, A., E. PRÉTET, and H. JOLIVET: Méthodes d'études de la corrosion des métaux et alliages par les gaz à température élevée et leurs applications (Methods for the Study of the Corrosion of Metals and Alloys by Gases at Elevated Temperatures, and their Applications), *Rev. Mét., Mém.*, v. 31, 1934, pp. 101–115; 186–191; 219–236.

1069. POWELL, R. W.: The Thermal and Electrical Conductivities of Metals and Alloys: Part I. Iron from 0 to 800°C., *Proc. Phys. Soc.*, v. 46, 1934, pp. 659–679.

1070. REBER, R. K.: The Effect of Nascent Hydrogen on the Magnetic Properties of Iron, *Physics*, v. 5, 1934, pp. 297–301.

1071. RUDER, W. E.: The Influence of Grain Size on Magnetic Properties, *Trans. Am. Soc. Metals*, v. 22, 1934, pp. 1120–1132.

1071*A*. SHELTON, S. M.: Thermal Conductivity of Some Irons and Steels over the Temperature Range 100 to 500°C., *National Bur. Stds. J. Res.*, v. 12, 1934, pp. 441–450.

1072. TÖDT, F.: Die Erhöhung der Auflösungsgeschwindigkeit des Eisens durch oxydierende und reduzierende Substanzen (The Increase in the Rate of Solution of Iron in the Presence of Oxidizing and Reducing Substances), *Z. f. Elektrochemie*, v. 40, 1934, pp. 536–541.

1073. TRONSTAD, L., and C. W. BORGMANN: Some Optical Observations on the Passivity of Iron and Steel in Nitric and Chromic Acids, *Trans. Faraday Soc.*, v. 30, 1934, pp. 349–361.

1074. TURNER, D.: Special Refractories for Metallurgical Research at High Temperatures, *Trans. Ceramic Soc.*, v. 33, 1934, pp. 33–55.

1075. VAN ARKEL, A. E.: Über die Herstellung von hochschmelzenden Metallen durch thermische Dissoziation ihrer Verbindungen (Production of High-melting Metals by Thermal Dissociation of Their Compounds), *Metallwirtschaft*, v. 13, 1934, pp. 405–408.

1935

1076. CHIPMAN, J., and D. W. MURPHY: Solubility of Nitrogen in Liquid Iron, Am. Inst. Min. Met. Eng., *Tech. Pub.* No. 591, *Metals Technology*, January 1935, 12 pp.

1077. DEAN, R. S., E. P. BARRETT, and C. PIERSON: Some Observations on Sponge Iron and the Properties of the Direct Steel Made from It, Am. Inst. Min. Met. Eng., *Tech. Pub.* No. 592, *Metals Technology*, January 1935, 9 pp.

1078. KELLEY, K. K.: Contributions to the Data of Theoretical Metallurgy. III. The Free Energies of Vaporization and Vapor Pressures of Inorganic Substances, U. S. Bur. Mines, *Bull., Preprint*, 1935, 400 manuscript pages.

1079. KELLOGG, D. R.: Electrodeposition of Iron for Wearing and Bearing Metal, *Metals & Alloys*, v. 6, 1935, pp. 97–99.

1080. MEHL, R. F.: Progress Report to the Metallurgical Advisory Committee of Carnegie Institute of Technology, February 1935, 13 manuscript pages.

1081. YENSEN, T. D., and N. A. ZIEGLER: Magnetic Properties of Iron as Affected by Carbon, Oxygen, and Grain Size, *Trans. Am. Soc. Metals*, v. 23, 1935, pp. 556–574.

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